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OFFICIAL PUBLICATION OF THE PROCEEDINGS, AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

American Dyestuff Reporter was founded in 1917 and the Textile Colorist and Converter (formerly Textile Colorist) was incorporated with it in January, 1949. Published every other Monday, by the **HOWES PUBLISHING COMPANY, INC.**, 44 East 23rd Street, New York 10, N. Y. **C. R. Howes**, President; **Ernest J. Finan**, Executive Vice-President; **Norman A. Johnson**, Vice-President & Treasurer; **Myron D. Reeser**, Vice-President; **Clara Patrick**, Secretary.

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AMERICAN
DYESTUFF REPORTER
DEVOTED TO TEXTILE WET-PROCESSING

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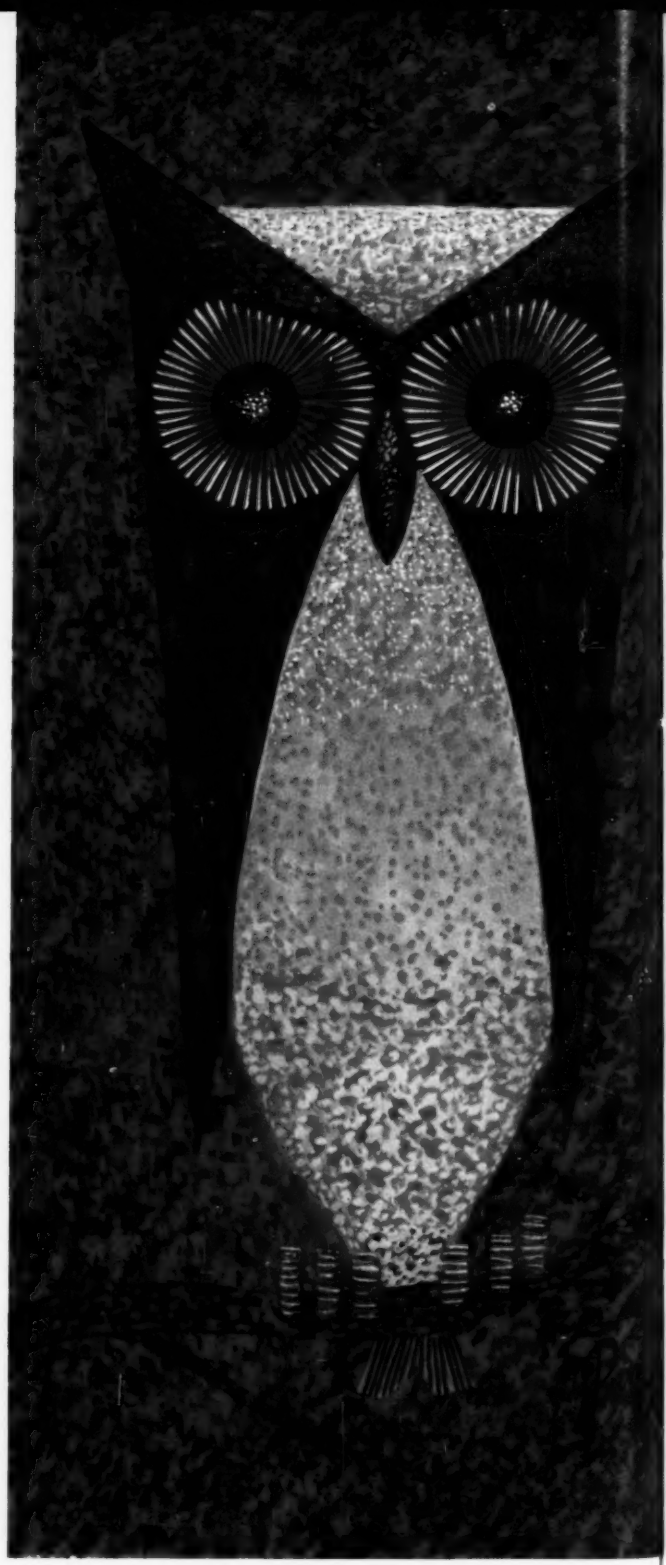

Continental's Golden Jet Service also includes Denver and Kansas City.

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THINKS AHEAD WITH TEXTILES

SANDOZ

AMERICAN
DYESTUFF REPORTER
Volume 48 July 13, 1959 Number 14

WHY DOES THE FLUORESCENCE OF OPTICAL BLEACHES REACH A LIMIT?

EUGENE ALLEN
American Cyanamid Co, Bound Brook, NJ

The fluorescence of optical bleaches on cloth reaches a limit at high concentrations of optical bleach. The reason is that almost all the available ultraviolet energy used for exciting the fluorescence is absorbed at high concentrations, and additional optical bleach cannot absorb any more. The shape of the fluorescence vs concentration curve on cotton cloth can be fairly well predicted on the basis of the Kulbelka-Munk reflectance law.

INTRODUCTION

IT is known that there is a concentration range of optical bleach on cloth beyond which an additional amount fails to give any great amount of additional fluorescence. Figure 1 shows typical curves of fluorescence plotted against concentration of optical bleach on the cloth. The leveling off of fluorescence at high concentrations is characteristic, and well known *(1)*. The purpose of this paper is to look into the reason for this effect.

THE PROCESS OF FLUORESCENCE

Optical bleaches function by absorbing ultraviolet radiant energy and re-emitting this energy at longer wavelengths as blue light. The mechanism by which the fluorescent emission causes a cloth to appear whiter has been discussed in previous papers *(2, 3)*.

A piece of cloth dyed with optical bleach does not absorb all the ultraviolet radiant energy which is directed on it. Some is reflected, and the reflected portion cannot contribute to fluorescence. The amount of ultraviolet radiation absorbed at each wavelength increases with the amount of optical bleach on the cloth. This is exactly analogous to the absorption of visual light by a dyed cloth, where the amount of light absorbed increases with the amount of dye on the cloth.

Furthermore, not all the absorbed ultraviolet energy may be converted to blue fluorescence. The factor, relating quanta of radiation emitted as fluorescence to quanta of radiation absorbed as ultraviolet energy is known as "quantum efficiency." A quantum efficiency of 1 means complete conversion of absorbed to emitted radiation. This is seldom obtained; more often quenching and other effects operate to decrease the quantum yield.

The leveling off of fluorescence at high concentration could, therefore, conceivably be caused either by a leveling off of absorption of ultraviolet energy or by a quenching effect leading to decreased quantum efficiency of fluorescence.

EXPERIMENTAL

Measurements of ultraviolet absorption, fluorescence and relative quantum efficiency were made by means of the Beckman Model DU spectrophotometer with reflectance attachment plus an auxiliary filter slide. The slide contained a filter capable of transmitting ultraviolet energy but no visual energy (Corning No. 5860). By means of the slide, the filter could be inserted at will between the sample and the phototube.

Ultraviolet energy at 360 mμ was used to irradiate the sample. Both the reflected portion of the ultraviolet radiation and visual fluorescent light left the sample, but with the filter in place only the reflected ultraviolet was seen by the photocube. When a cloth dyed with optical bleach was run against an undyed cloth as reference, this type of measurement gave a percent reflectance reading, R. Subtracting the reflectance from 100 gave directly the percent ultraviolet radiation absorbed by the optical bleach in the sample. The percentage of radiation absorbed was called absorptance, symbol A; $A = 100 - R$.

A similar measurement of the dyed sample against undyed cloth but with the filter removed gave a reading corresponding to both the reflected and fluorescent light. Subtracting the percent reflected light, R, from this value gave a reading corresponding to relative fluorescence, called F. It should be carefully noted that this F value does not represent the absolute percentage of incident ultraviolet energy converted to fluorescence. The reason is that the fluorescence is given off at a different set of wavelengths; this brings into play differences in energy per quantum of radiation, in phototube sensitivity, and in light scatter. A factor must be introduced to correct for these three effects if absolute values are wanted. Since this factor is the same for the same optical bleach, the F values may be used as an indication of relative fluorescence as a function of concentration of any one optical bleach, which is just what is wanted here; but the F value of one whitener cannot be directly compared with that of another whitener unless the factors are applied.

Similarly, the ratio F/A (indicating fluorescence per energy absorbed), called Q, may be used as an indication of quantum efficiency. For the reasons given above, the Q values so obtained are not absolute quantum efficiencies, and not even relative values in the comparison of one whitener against another. However, they are relative values in the sense that they show how the quantum efficiency varies with concentration for any one whitener, which is what is desired in this work.

Dyeings of two different optical bleaches were made on cotton. A typical red-shade optical bleach and a typical green-shade optical bleach were used; the former will be designated as Whitener 1, and the latter as Whitener 2. Both of these whiteners were known to exhaust almost completely from the bath. Dyeings of each whitener were made in concentrations ranging from 0.010% to 0.400% on the weight of the cloth.

SANDOZ

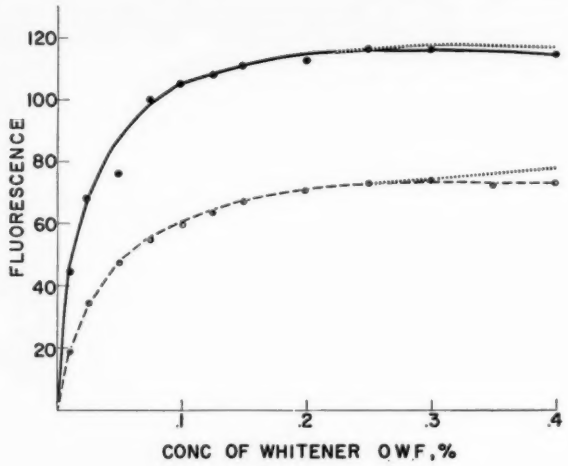

Figure 1
Curves of fluorescence against concentration for Whiteners 1 (solid line) and 2 (dashed line). The dotted portions of each curve represent hypothetical fluorescences which should be obtained if the Kubelka-Munk law were obeyed.

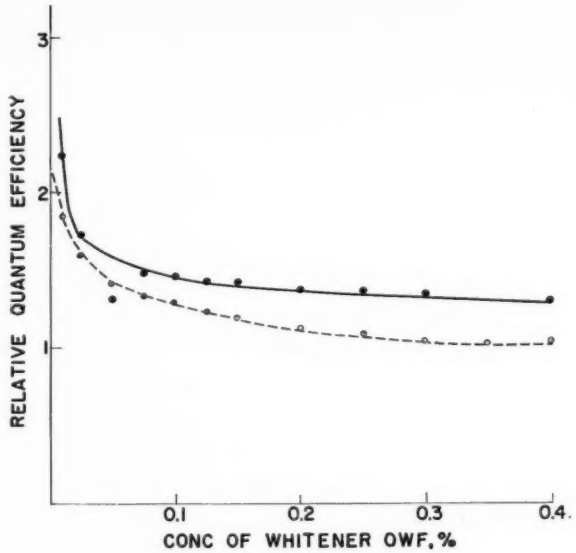

Figure 3
Curves of relative quantum efficiency against concentration for Whiteners 1 (solid line) and 2 (dashed line).

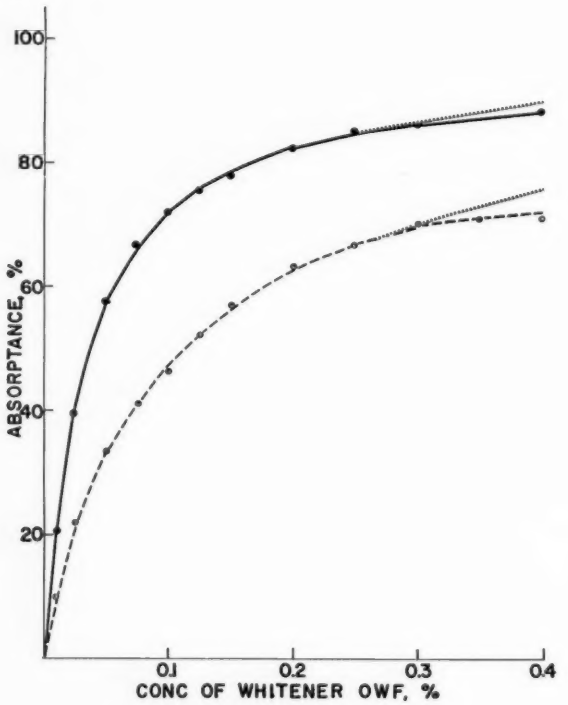

Figure 2
Curves of absorptance against concentration for Whiteners 1 (solid line) and 2 (dashed line). The dotted portions of each curve represent hypothetical absorptances which would be obtained if the Kulbelka-Munk law were obeyed.

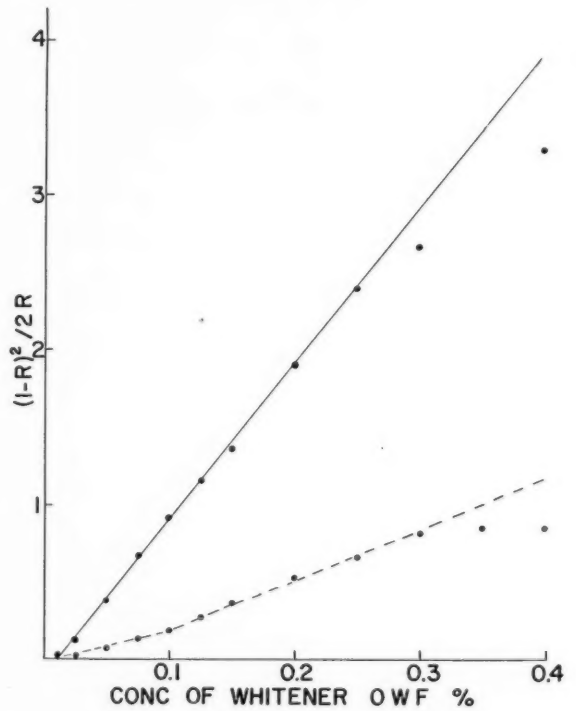

Figure 4
Plots of Kubelka-Munk function against concentration for Whiteners 1 (solid line) and 2 (dashed line).

Two thicknesses of cloth were used for each reading, and each dyeing was measured at eight different places and the readings were averaged.

The Beckman instrument was equipped with a photomultiplier tube, which gave adequate precision for the work. In the case of the readings with the filter removed, the instrumental values for the dyed cloths were higher than those for the undyed cloths, and therefore the readings were taken in reverse order; ie, the balance was effected against the dyed cloth and the readings were taken on the undyed cloth. The reciprocal of the resulting reading was used for the calculation.

RESULTS

Curves of F (relative fluorescence), A (absorptance), and Q (relative quantum efficiency) plotted against concentration of optical bleach on cloth are shown in Figures 1, 2 and 3. Looking at the quantum efficiency curve in Figure 3 first, we see that the efficiency of conversion drops off sharply with increasing concentration at the low concentrations, and very gradually at the high concentrations. However, it is precisely those high concentrations which interest us at the moment; since Q can be considered to be fairly constant toward the right of the curves, variation in Q cannot account for the failure of fluorescence to increase with concentration in this region. Therefore, it seems that the quenching effect is not the main determining factor.

Looking now at the absorptance curves in Figure 2, we note that the percent absorptance goes up sharply at the lower concentrations and begins to level off at the higher concentrations, approaching 100% as the limit—this simply means that there is no more ultraviolet energy to be absorbed. It is interesting that the absorption of ultraviolet radiation seems to obey the Kubelka-Munk law of reflectance, as is shown in Figure 4. In these graphs, the function $(1 - R)^2/2R$ instead of A is plotted against concentration. Obedience to the Kubelka-Munk law demands straight lines in these plots, and for all save the highest two or three concentrations approximately straight lines are obtained. The failure of the Kubelka-Munk law at the highest concentrations has very little effect on either the absorptance or fluorescence. The dotted lines in Figure 2 show the absorptance values which would be obtained if the Kubelka-Munk law held at the highest concentrations. Similarly, the dotted lines in Figure 1 show the corresponding fluorescence which would be obtained from these slightly higher absorptance values. It is seen that very little increase of fluorescence would result if the samples had obeyed the Kubelka-Munk law.

Figure 2 shows that, although the absorptance of Whitener 2 has started to level off at the higher concentrations, the absorptance curve is still not too near the limit of 100%. It might be argued from this that considerably more fluorescence would be possible if the concentration of optical bleach were still further increased. However, it would take a prohibitively large amount of additional whitener to give an appreciable increase in fluorescence. It can be calculated on the basis of the Kubelka-Munk law that an additional absorption of 10% more light (resulting in a corresponding increase of 10% in fluorescence) would require about 70% more whitener. Since the Q curve would probably be dropping faster than the A curve would increase, there would be a maximum in the F curve; evidence of this is seen in Figure 1 and, in fact, has frequently been observed. (*1*)

It therefore appears that the reason that the amount of fluorescence approaches a limit at the higher concentrations of optical bleach is simply that the absorption of ultraviolet radiant energy approaches a limit at these same concentrations. The limit is 100% of the available ultraviolet energy, and additional optical bleach cannot absorb any more ultraviolet because there is no more to absorb. The shape of the fluorescence vs concentration curves in Figure 1 can be fairly closely predicted on the basis of the Kubelka-Munk reflectance law; it is not known if optical bleaches would follow this law on other fabrics, however.

This behavior is not surprising or unusual because many colored dyes behave in exactly the same way. Considering a blue dye, we know that at very low concentrations small increments of dye produce a fairly large effect on the color of the fabric. However, at high concentrations, a point is reached at which further additions of dye have no further effect on the color. In this region, the color is black; practically all the light reaching the sample is absorbed, and additional dye cannot absorb any more.

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(*3*) Allen, E, *Am Dyestuff Reptr* **46**, 425-432 (1957).

General Calendar

AMERICAN OIL CHEMISTS SOCIETY
Sept 28-30 (Statler Hotel, Los Angeles, Calif)

AMERICAN TEXTILE MACHINERY ASSOCIATION
May 23-27, 1960 (American Textile Machinery Exhibition, Auditorium, Atlantic City, NJ)

ASSOCIAZIONE COSTRUTTORI ITALIANI DI MACCHINARIO PER L'INDUSTRIA TESSILE
September 12-21 (3rd International Textile Machinery Exhibition, Milan Fair, Milan, Italy)

DRUG, CHEMICAL AND ALLIED TRADES SECTION, NY BOARD OF TRADE
Sept 17-20 (69th Annual Meeting, Sagamore Hotel, Bolton Landing, Lake George, NY)

GORDON RESEARCH CONFERENCE ON TEXTILES
July 13-17 (Colby Jr College, New London, NH)

NATIONAL COTTON COUNCIL
Oct 7 (Chemical Finishing Conference, Mayflower Hotel, Washington, DC)

SYNTHETIC ORGANIC CHEMICAL MANUFACTURERS ASSOCIATION OF THE UNITED STATES
Sept 15, Oct 13, Nov 4 (Luncheon meetings at the Hotel Roosevelt, New York, NY); Dec 2 (Annual meeting and dinner—Hotel Roosevelt, New York, NY)

TEXTILE RESEARCH INSTITUTE
March 24-25, 1960 (30th Annual Meeting, Hotel Commodore, New York, NY)

THE CONTINUOUS CARBAMOYLETHYLATION OF COTTON FABRIC: PRELIMINARY COST STUDY

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J D GUTHRIE, and E F POLLARD
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New Orleans, La

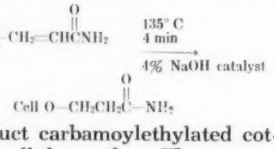
INTRODUCTION

IN their search for new cotton products, scientists at the Southern Regional Research Laboratory carbamoylethylated cotton fabric by impregnating it with an aqueous solution containing acrylamide and an alkaline catalyst, followed by heating in an oven (3). They produced a chemically modified cotton having substantial heat resistance, a slight degree of rot resistance, and good retention of strip breaking strength. The carbamoylethyl groups were found to be stable to hydrolysis under standard laundering conditions. The affinity of carbamoylethylated cotton for Pontamine Fast Blue RRL 175† (CI Direct Blue 67) and its increased affinity for vat dyes were also observed.

Partial conversion of the carbamoylethyl groups to aminoethyl groups was achieved by moistening with sodium hypochlorite solution, and then drying.

REACTION AND PROCESS

The reaction of cotton and acrylamide is a Michael-type addition reaction and is illustrated as follows:



The product carbamoylethylated cotton, is a cellulose ether. The process described in this cost study was applied on a small pilot-plant scale. 48 x 48 cotton sheeting was padded to a wet pickup of 89% with a solution containing, on a weight basis, 50% acrylamide, 4% sodium hydroxide, and 46% water. Reaction was allowed to continue in an oven at 275° F for four minutes, after which the fabric was washed with water, and dried. Total weight add-on of the product was 10.9%, and nitrogen content was 2.39%, corresponding to a substitution of approximately one carbamoylethyl group per three anhydroglucose units.

COSTS

This cost study is based on continuous operations in a new hypothetical plant, at a fabric processing rate of 120 yards per minute. Figure 1 is a material balance-flow diagram for these continuous operations. Annual productions were varied by operating the hypothetical plant for one, two, and three shifts for 250 days per year, and for three shifts for 350 days per year.

INVESTMENT COSTS

Installed equipment costs, shown in Table I, are estimates based largely on costs obtained from manufacturers for individual equipment units for continuous processing at the specified rate.

TABLE I
Continuous carbamoylethylation of cotton fabric[1]: Installed equipment costs

Equipment unit description	*Installed cost Dollars*
Three-roll padder	5,540
Oven drier, roller-type	126,224
Washing range (eight sections)	197,000
Tenter frame, 90' long	80,689
Two mixing tanks, 3400 gal each	21,000
NaOH storage tank, 5000 gal [2]	9,520
Pumps	2,221
All units	442,194

[1] 48 x 48 cotton sheeting, 60" wide, eight ounces per linear yard, at rate of 120 yards per minute.
[2] For operating one shift for 250 days per year, NaOH storage tank would be approximately $3,000 less.

TABLE II
Continuous carbamoylethylation of cotton fabric: Investment costs Plant capacity——60,480,000 yards/year

	Dollars
a) Installed equipment	442,194
b) Process piping (13% of "a")	57,485
c) Instrumentation (2% of "a")	8,844
d) Outside lines (3% of "a")	13,266
e) Auxiliary facilities	60,000
f) Buildings	228,951
g) Total physical plant cost	810,740
h) Engineering and construction (20% of "g")	162,148
i) Contingencies (15% of "g")	121,612
j) Total plant cost[1]	1,094,500

[1] For operating one shift for 250 days per year, total plant cost would be approximately $15,800 less.

Investment costs for the hypothetical plant are given in Table II. Percentages applied to the total installed equipment cost in estimating process piping, instrumentation, and outside lines, were selected from published information (*1, 2, 4,* 5). Auxiliary facilities include a steam boiler having a capacity of 25,000 pounds of 60 psig steam per hour.

A building was included having a steel frame, brick and concrete walls, and a concrete floor and roof. Both areas, manufacturing and warehouse, are provided with heating, lighting, and sprinklers. In addition, the manufacturing area has ventilation, sanitary plumbing, and chemical-resistant tile. Building cost was derived using a unit cost of $21.50 per square foot of floor area for the manufacturing area, and $8 per square foot for the warehouse area. Area requirements were estimated from equipment specifications, with provision for reasonable working space around the equipment.

Engineering and construction costs, and contingencies were estimated at 20% and 15%, respectively, of total physical plant costs, and were included in total plant costs.

The investment costs of Table II are for a new installation, and would not be applicable for processors who already have the usual resin-finishing equipment needed for this process. For such a processor, who might consider the carbamoylethylation of cotton intermittently with other chemical processing, additional plant investment would be unnecessary.

PROCESSING COSTS

Processing costs are itemized in Table III.

CHEMICALS——Chemical costs were calculated from chemical requirements, indicated in Figure 1, and current prices. From Table III, it can be seen that chemical costs are the largest single cost. Unit prices used were 29 cents per pound for acrylamide and 2.9 cents per pound for 50% liquid sodium hydroxide, 76% Na_2O basis.

* One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, US Department of Agriculture.

† This tradename is given as part of the exact experimental conditions and not as an endorsement of the product over those of other manufacturers.

LABOR———Labor costs are estimated as those applicable to a textile finishing plant, with skilled labor at $2.35 per hour and semiskilled labor at $1.62 per hour. Double time was allowed for weekend work and a 10 percent night differential was used for second- and third-shift operations.

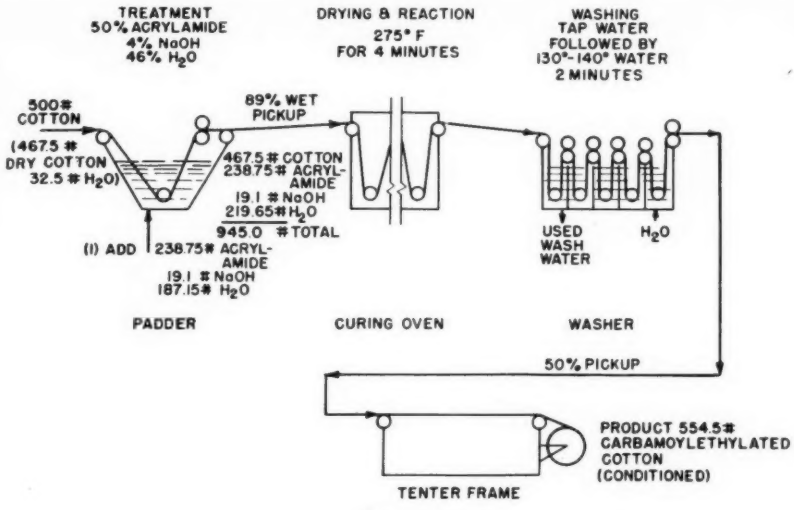


Figure 1
Continuous carbamoylethylation of cotton fabric
1000 yds - 48 x 48 fabric, 60" wide, eight oz/linear yd

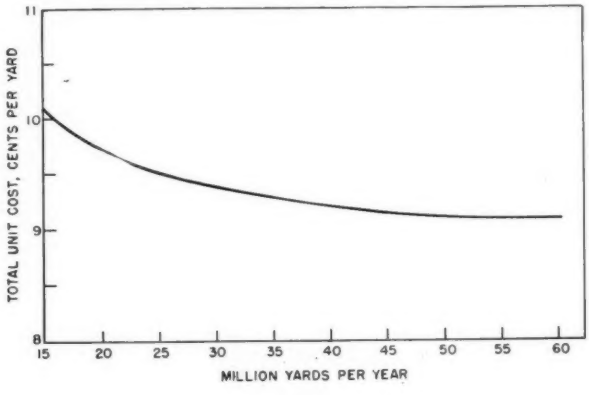


Figure 2
Processing costs for carbamoylethylating cotton fabric
(48-square sheeting, 60" width, to 2.39% N)

TABLE III

Continuous carbamoylethylation of cotton fabric: Processing costs and general expenses

Annual Production (1000 yards)	14,400[1]	28,800[2]	43,200[3]	60,480[4]
Total Plant Cost (dollars)	1,078,700	1,094,500	1,094,500	1,094,500
Processing Cost:				
Direct costs (¢/yd):				
Chemicals	6.98	6.98	6.98	6.98
Labor	0.13	0.14	0.14	0.18
Utilities	0.16	0.16	0.16	0.16
Other	0.30	0.15	0.10	0.08
	7.57	7.43	7.38	7.40
Indirect costs (¢/yd): (Payroll overhead, general plant overhead, control laboratory, and packaging costs)	0.20	0.17	0.16	0.17
Fixed costs (¢/yd): (Insurance, taxes and depreciation)	0.63	0.32	0.21	0.15
Contingencies (¢/yd):	0.42	0.40	0.39	0.40
General Expenses (¢/yd):	1.35	1.11	1.03	0.99
(Gen admn and overhead, financing, and sales costs)				
Total (¢/yd)	10.17	9.43	9.17	9.09
(¢/lb product)	18.31	16.97	16.51	16.36

[1]One-shift, 250-day operation
[2]Two-shift, 250-day operation
[3]Three-shift, 250-day operation
[4]Three-shift, 350-day operation

UTILITIES———Utility costs included those for steam, electrical power and process water. Unit costs used were 70 cents per 1000 pounds of steam; one cent per kilowatt-hour of electricity; and 25 cents per 1000 gallons of water.

FINANCING———Financing costs were calculated using an interest rate of five percent per annum on total capital, which is the sum of total plant investment and working capital.

TOTAL PROCESSING COST———The total cost for carbamoylethylating 48 square cotton sheeting, 60" wide, eight ounces per yard of untreated fabric, to a weight add-on of 10.9% and a nitrogen content of 2.39%, ranged from 10.2 cents per yard at an annual production of 14.4 million yards, to 9.1 cents per yard at an annual production of 60.5 million yards. In Figure 2, total unit processing costs from Table III are plotted versus annual production. These costs are exclusive of the cost of cotton used, and are for custom processing without profit.

SUMMARY

This cost study shows that, at an annual production of 60,480,000 yards, cotton can be carbamoylethylated by a continuous method at a cost of 9.1 cents per yard or 16.4 cents per pound of product. Because the process can be accomplished in the usual equipment for resin finishing, these processing costs and others in Table III would apply to any carbamoylethylation at the specified rate that might be done intermittently with other chemical processings in the same equipment. Since the processing costs are based on a new installation, they could be less by as much as the depreciation cost in plants having fully depreciated equipment of the type needed. Depreciation cost represents about 65 percent of fixed cost. The continuous carbamoylethylation process might be particularly attractive to a processor who would want to add another cotton product with special characteristics to his line.

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IMPORTANT FACTORS TO CONSIDER WHEN SELECTING WATER-SOLUBLE GUMS

CHARLES M FERRI

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New York, NY

NATURAL water-soluble gums play an important role as binders, thickeners, film-formers, emulsifiers or stabilizers. Countless products that utilize water as a base can be enhanced through the use of a vegetable gum or derivative. Their versatility carries them into numerous successful operations, eg, in the textile industry as printing pastes, stiffening agents, sizes, etc. Their continued use and newer applications are limited only by technical and consumer ingenuity. Yet, because a gum is only one of a number of materials that form the finished product, the manufacturer usually has only a limited knowledge of gum properties and their variations and how they affect his product. This situation is basically due to the extremely large list of processed gums available, some developed only recently, which has made it impractical for the manufacturer to do adequate development work with this myriad of materials.

Regardless of the complexity of the subject, the gum user has to select the best type, grade and form of gum from the standpoints of economy, manufacturing performance,

Charles M Ferri

and quality of end product. Fortunately, he has been relieved of much of the responsibility by those leading gum suppliers who are equipped to import and process gums on a scientific basis. These suppliers can furnish gums of a uniform quality at a relatively stable price and make valuable recommendations to the manufacturer. However, the final choice rests with the user, and he owes it to himself to consider several important factors when he must select a water-soluble gum for his product. By determining his precise needs, then consulting with his supplier, the gum user can be confident that he has chosen the right gum from the host of materials available to him.

FUNCTION OF SUPPLIER —— An important part of the supplier's responsibility lies in eliminating gum variation through proper sorting and classification. For example, seasonal variations will affect the properties of most water-soluble gums. If gum arabic is gathered during the late season (November through February), it will have different properties than the same gum gathered from March through June. In this case, the most important property change is bodying effect or viscosity. However, this variation does not necessarily mean that one of these types is superior. The properties of either type may be desirable for a specific use. The reliable supplier should have sufficient stocks of each type on hand to meet the demands of the user during *all* times of the year. Seasonal variations also may affect other gums, such as tragacanth, karaya, locust bean, and guar.

Figure 1
Mesh size plays an important role in clarity of the gum solution. Granular gum arabic (left) forms almost clear solution while gum arabic powder (right) yields a much darker, opaque solution. Very fine mesh sizes also destroy some of the viscosity characteristics of the gum.

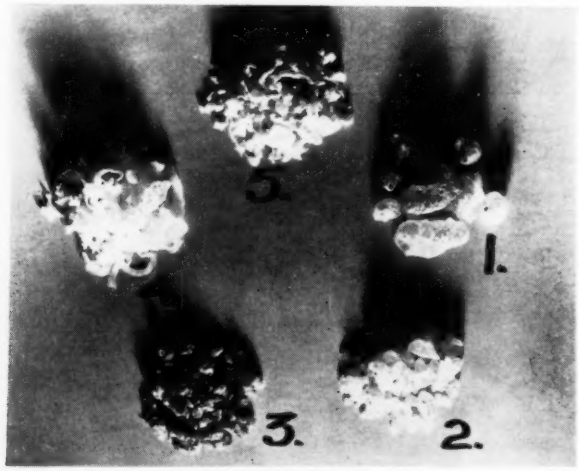

Figure 2
Unprocessed gums are a rare sight to the user, who usually needs the larger degree of control offered by processed gums. Raw gums shown above are: 1) gum arabic (Selected Sorts); 2) gum karaya (No. 1 WSGA); 3) gum karaya (No. 3 WSGA); 4) gum tragacanth (No. 1 Ribbon); and 5) gum tragacanth (No. 27 Flake).

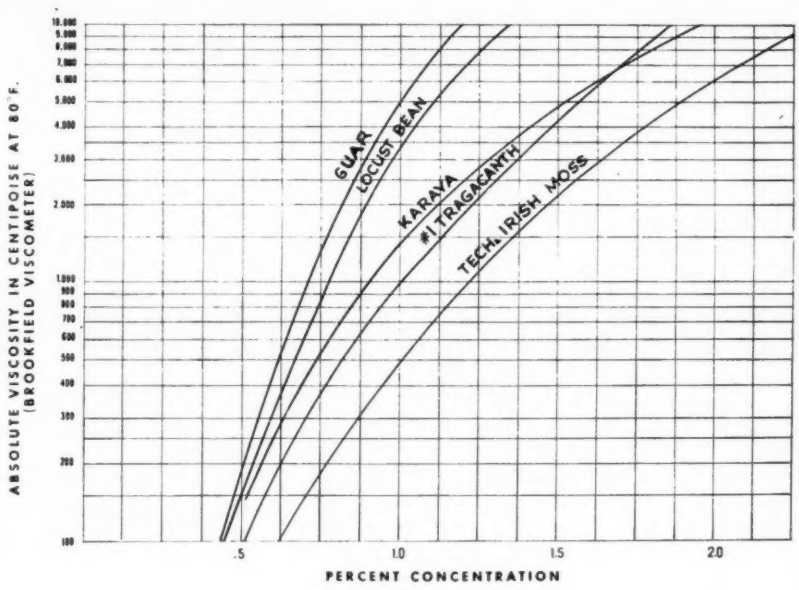

Figure 3
Chart shows typical viscosities of various gums according to percent concentration. Viscosity is a very important factor in the function of all gums except gum arabic.

Figure 4
Viscosity of gum solution is measured with a Brookfield Viscosimeter and the result is given in centipoises. Uniformity of viscosity and desired bodying at minimum concentrations are important considerations to the user.

In addition to viscosity, other properties affected by seasonal variation include: color, insolubles and moisture content. Specific constituents, such as metallic compounds and enzymes, must often be taken into consideration by users who require uniformity in certain chemical properties for some special reasons. By careful purchasing, preliminary inspection in the growing area, and scientific milling and blending, the reliable supplier completely eliminates seasonal variations in natural gums.

Price stability constitutes another factor for which the gum supplier is responsible. By combining well-organized purchasing methods and adequate storage facilities, he can purchase large quantities of a particular gum at the most opportune time. As a result, the gum user can depend on the supplier to furnish uniform gums, within specifications, at a stable price any time of the year.

GUM COLOR ——— A number of other possible variations are also the responsibility of the supplier. The gum user has to give detailed consideration to these possibilities to get the best gum for his needs. One of these factors is color, an attribute that varies in importance depending upon the gum in question. For example, the color of grains or powders of equal mesh size are an indication of the purity of gum arabic and karaya. The lighter the color, the cleaner the gum. With tragacanth, guar, and locust bean gums, the darker powder usually has a lower viscosity. The color variations in gum arabic and karaya are caused by differences in the time of gum gathering. Those gums gathered close to, or during, the rainy season contain a higher percentage of insolubles. In guar, locust bean, and tragacanth, color variations are a result of the type of seed collected or exudation gathered.

In those end products where color is important, proper selection of either a powdered or granular material is necessary to insure the required color. With gum arabic, for example, a light, clear, amber color is better obtained with a granular than with a powdered gum. When gum tragacanth is used in translucent end products, the choice should be a whole or granular type of ribbon rather than a powder.

IMPORTANCE OF MESH SIZE ———Mesh is another important factor with which the gum user should be concerned. It plays an important role in color, solubility, clarity of solution, and filtration characteristics of the finished product (Fig 1). The manufacturer should generally avoid the very fine mesh sizes, which usually yield darker solutions, and where some of the viscosity characteristics of the gum itself are destroyed. The reliable gum supplier processes gums so that there is a minimum loss of viscosity.

When the user filters the solution, particularly when gum arabic is used, it is advantageous to use coarse meshes. These fast-filtering types save time and cut labor costs. In some cases, it may be advantageous to use a top grade of powdered gum arabic, which contains as low as .04% insolubles and may be pure enough to eliminate the need for filtration.

Some suppliers are equipped to furnish gums within a closely controlled range of mesh sizes. As a result, the user gets the advantages of better wettability, minimum dusting during processing, and maximum uniformity of blends when the gum is sold in a dry mix.

CHOOSING WHOLE OR PROCESSED GUMS———The gum user also has the choice between a whole gum in lumps, flakes, or ribbons (Fig 2) or a processed gum. A processed gum gives the user a much greater degree of control than is possible with a whole unprocessed gum. However, if the basic consideration is low cost, which necessitates the use of an unprocessed gum, the manufacturer must make the following sacrifices: 1) limited standardization of end product, 2) relatively high percentage of impurities, 3) increased processing time.

Figure 5
Gum dust can cause a problem by settling on floors, equipment, and products. Problem and solution are illustrated above with two drums of gum arabic powder: fine powder (left) exhibits high degree of dusting, while coarser powder (right) produces very little dust under the same conditions.

IMPORTANCE OF UNIFORM VISCOSITY —— Viscosity is an important factor in all gums except gum arabic (Fig 3). Although there is justifiable stress on high-viscosity gums at the lowest price, it is just as important to consider the factor of uniform viscosity. When the user has incorporated a certain type and grade of gum for a length of time, his formulation is finally adjusted to this particular grade. Uniformity of viscosity then assures the constant usefulness of the formulation. The manufacturer should strive to use a gum that produces the desired body at minimum concentration (Fig 4). At this point, it becomes the supplier's responsibility to furnish this particular gum within a narrow range of bodying limits.

Although the viscosities of different types of gums may be similar, flow characteristics may differ radically and impart significant changes to the finished product. For example, karaya will yield viscous solutions of either a ropy or short-flow type. Tragacanth, on the other hand, will produce viscous but smooth-flowing solutions. The end use of the product alone should determine the type of gum to use.

GUM PURITY —— Purity may be a very important consideration, depending upon the type of product in which the gum is incorporated. It is usually indicated by a low percentage of insolubles, and light color. Gum arabic and tragacanth are covered under U S Pharmacopeia requirements. Karaya is covered under National Formulary specifications. USP and NF specifications serve to protect the user by setting minimum standards. However, a reliable supplier will make every effort to furnish gums at standards well above the minimum. For example, USP requirements for gum arabic call for a maximum of 1% insolubles content. However, reliable gum suppliers will furnish gum arabic with insolubles content as low as .03%. Another example is gum karaya, where the NF specification for insolubles content is 3% maximum. Certain grades of karaya can actually be supplied with insolubles content as low as 0.1%. Certain industrial uses may require maximum purity from the standpoint of production.

DUSTING PROBLEMS —— In some types of production, powdered gums may cause a difficult dusting problem. When a barrel of gum is dumped into a solution or process, the dispersed dust particles may seriously interfere with plant operations. Dusting can be minimized by the proper selection of mesh size of the gum (Fig 5).

PRESERVATIVE REQUIREMENTS —— In most cases, the gum user must provide preservatives for his product. Most gums, either natural or synthetic, will support bacteria or mold growth. The degree of mold or bacteriological breakdown will vary with the different types of gums. One of the most resistant to spoilage is gum tragacanth, particularly when it is used in conjunction with glycerin or propylene glycol. With most gums, a 0.1% content of a preservative, such as benzoate of soda, phenol, or commercially available phenol derivative, is usually successful. This 0.1% content should be based on the total weight of the finished product.

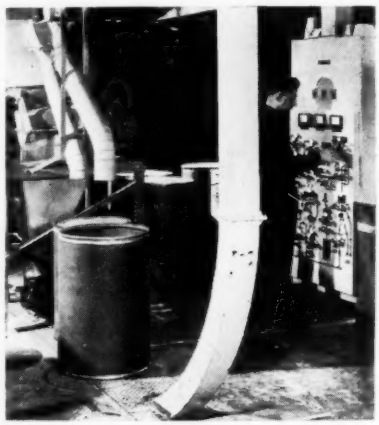

Figure 6
Modern gum processing equipment at Morningstar's Hawthorne, NJ, plant, includes control panel (right), with glow sheet on its face, which permits complete operation of the system from this single location. A number of these units are located on each floor of the plant.

CUSTOM-MADE GUMS —— The trend in the gum industry has been to prepare custom gums to fit specific industries. To derive the greatest amount of benefit, the gum user should maintain a closer contact with the technical department of his supplier. For example, should the user make any changes in the ingredients contained in his finished product, he may require a change in the form of gum used. Those suppliers equipped with broad technological know-how and up-to-date equipment have been at the head of the custom-gum trend. For example, some of the equipment now commonly used at the Morningstar-Paisley gum plant in Hawthorne, NJ, for the standardization of gums includes reflectometers, spectrophotometers, pH control equipment, and modern viscosity meters, in addition to modern processing equipment (Fig 6). This trend in specialization has brought forth an improved line of water-soluble gum products, which conform to the most exacting specifications of the technical industries.

TABLE I
Background of water-soluble gums used in the textile industry

Gums	*Type*	*Botanical origin*	*Country of origin*
Arabic	Soluble, nonswelling	Trees . . . Species Acacia Vereb	Sudan
Tragacanth	Cold-water swelling	Plants . . . Species Astragalus	Iran, Syria, Turkey
Karaya	Cold-water swelling	Trees . . . Sterculia Urens	Southern Asia, India
Locust bean	Swelling with heat	Seeds . . . Ceratonea Siligua	Mediterranean area & Northern Africa
Guar	Cold-water swelling	Seeds . . . Cyamopsis Tetragonoloba	India

Proceedings of the

American Association of Textile Chemists and Colorists

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July 13, 1959

Piedmont Section———

RELATION OF DYE STRUCTURE TO PROPERTIES OF DISPERSE DYES*

Part I—Anthraquinone Blues

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A series of blue anthraquinone dyes synthesized by condensation of aromatic amines with dinitro anthrarufin, dinitro chrysazin or their mixtures has been evaluated as to colorfastness and dyeing properties. Variations in structure have been related to these properties.

Resistance to gas-fading change on acetate fibers is shown as characteristic of dyes which do not contain vulnerable aliphatic amino groups.

Correlation is shown in this series between structures which are resistant to gas fading and those which show good lightfastness on polyester fibers. Dyeing specificity is shown between polyester fiber and acetate fiber with the more hydrophobic structures showing better affinity for polyester fiber.

The use of isomeric mixtures of dyes is shown to give increased dyebath stability and higher exhaustion.

Dyeing properties are related to basic principles of particle size in dyebath, solubility of dye in water phase, and diffusion rate into specific fiber.

INTRODUCTION

DISPERSED blue dyes of anthraquinone structure have been used since the introduction of acetate fibers. Their deficiency with respect to atmospheric change due to oxides of nitrogen has led to considerable work with the objective of finding structures which are completely resistant or of improved resistance to this type of color change known as gas fading.

This search for anthraquinone blues of increased fastness received additional impetus with the introduction of polyester fibers. The conventional blue anthraquinone dyes show excellent affinity for polyester fiber but unusually poor lightfastness. Although atmospheric fading due to oxides of nitrogen is not a problem of polyester fiber, the poor lightfastness prevents the use of the conventional 1-4 dialkyl amino anthraquinone blue dyes on Dacron polyester fiber.

With the advent of Arnel cellulose triacetate fiber and consumer demand for combination of atmospheric fading resistance and higher wash- and lightfastness, the need for anthraquinone blues with the desired combination of properties was further emphasized. The problem of the dye chemist in finding new disperse dye structures which would be colorfast on acetate, triacetate, and polyester fiber is further complicated by the requirements of the dyer that the new dyes possess practical dyeing properties, such as stable dyebath dispersion, satisfactory dyeing rates, and good intrinsic affinity for the fiber.

The work herein described is based on dye syntheses and the study of the dyeing properties of the individual dyes as carried out in the Celanese Research Laboratories by the authors. The principles used in formulating the dye structures for syntheses which gave improved colorfastness are a) dyes based on ortho substitution to reduce reactivity of vulnerable amino groups, and b) dyes based on structures containing only resistant arylamino groups.

The analysis of the dyeing properties of each specific dye is based on the now generally accepted principles of dispersed dye behavior:

1) that the mechanism of dyeing of dispersed dye is one of solid solution,

2) that dyes dissolve in the aqueous dyebath and are absorbed from the water by the fiber, and

3) that dyeing rates and pile-on are dependent on both the specific dye structure and the particular fiber.

EXPERIMENTAL AND DISCUSSION

CONSIDERATIONS LEADING TO THE SYNTHETIC APPROACH ———The synthesis of a disperse blue dyestuff with satisfactory dyeing properties for secondary acetate and with a high level of fastness to both light and gas fading has long been an objective of research in the field of disperse dyes. Quite early in the work on secondary acetate, it was found that both azo and anthraquinone structures have affinity for this fiber. For example, both Celliton Blue B (1-methylamino-4-hydroxyethylamino anthraquinone), and Setacyl Blue G (2-4-dinitro-6-chlorophenyl azo-4′-dialkyl amino 5′-methoxy-2′-acetamino benzene) dye acetate heavy shades of blue. Both these compounds are good dyestuffs with acceptable dyeing properties, producing dark, level blue dyeings at a satisfactory rate from a stable dyebath. However, in neither instance are the fastness properties completely satisfactory. Blue azo structures tend to be particularly sensitive to light, and the level of lightfastness that can be obtained with this particular azo

* Presented by V S Salvin before the Piedmont Section at Winston-Salem, NC on April 11, 1959.

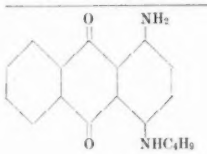
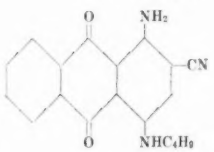
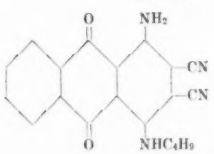
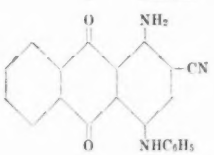
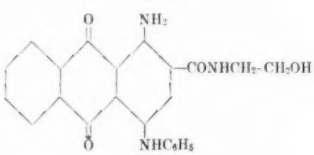
compound is such that its use is limited to linings and other fabrics that are not exposed to much light during service. Although 1-methylamino-4-hydroxyethylamino anthraquinone is relatively resistant to the changes caused by exposure to light, it presents another important fastness problem. Secondary acetate dyed with this compound tends to redden during service. The change is quite different from the one caused by light and it occurs much more readily in industrial than in rural areas. This same type of reddening can be brought about in the laboratory by exposing the fabric to the fumes produced by burning a gas flame, and consequently it is called gas fading. These observations indicate that, in order to obtain a dyestuff with acceptable dyeing properties, either 1) the azo structure has to be rendered fast to light, or 2) the anthraquinone structure has to be made gasfast. Although lightfast azo reds have been obtained, attempts to produce azo blues of lightfastness have not proved successful despite the use of the newer intermediates. In view of this and of the satisfactory overall dyeing properties of 1-methylamino-4-hydroxy-ethylamino anthraquinone, many attempts have been made to produce an anthraquinone structure that would retain the dyeing characteristics of this derivative and yet would be resistant to gas fading.

CHEMICAL NATURE OF GAS FADING——A knowledge of the nature of the causative agent is a necessary prerequisite to the synthesis of an anthraquinone structure that resists gas fading. The original work on this aspect of the problem revealed that the oxides of nitrogen present in the atmosphere are responsible for the changes in color *(1, 2)*. More recently, it has been shown that, specifically, nitrogen dioxide is the active agent (3). This gas is very soluble in the acetate fiber, and indeed this fiber can be used to concentrate the gas from the atmosphere. Consequently, when acetate fabrics dyed with 1-methylamino-4-hydroxy-ethylamino anthraquinone are exposed for a prolonged period of time to an atmosphere containing as little as two parts per 100 million of nitrogen dioxide, they will show a significant color change. A much higher concentration than this is found in most industrial areas and thus gas fading does present a problem. The AATCC chamber for testing this fastness property contains nitrogen dioxide in a concentration of two parts per 100,000 obtained as the combustion product of a gas flame. After twenty-four hours at this level of exposure, a large proportion of the anthraquinone blue in a test ribbon has been destroyed. Diazotization of a primary amino group, nitrosation of a secondary amino group and oxidation have been proposed as possible mechanisms for the reaction between nitrogen dioxide and the various alkylamino anthraquinones *(1, 2)*. Recently, Couper *(4)* isolated a number of the degradation products formed by the gas fading of 1,4-dimethylamino anthraquinone. The structure of these products emphasized the role played by oxidation and indicated other reactions, such as dealkylation, deamination, and the replacement of the amino by a hydroxyl group. Regardless of the exact mechanism whereby these anthraquinone blues are converted to mixtures of deaminated, dealkylated reddish structures, it is known that the point of attack is the alkylamino group and that the active agent is nitrogen dioxide. Therefore, the way to control gas fading is to reduce the reaction between nitrogen dioxide and the alkylamino group or amino group.

One means of interfering with the reaction between nitrogen dioxide and the dyestuff is to apply a chemical to the fabric which will react with nitrogen dioxide at a faster rate than the dyestuff. Such a compound has to fulfil a number of requirements: it must be easy to apply; it must have a fair degree of permanency; it must not discolor in the light or reduce the lightfastness of the dyestuffs; and it must react readily with nitrogen dioxide without producing a colored product. As the result of a thorough investigation of

TABLE I

Ortho-substituted blue anthraquinones

Structure	Affinity & pile-on	Gas-fading change after	
		One AATCC unit	Two AATCC units
	very good	2	1
	good	4	3–4
	poor	5	4
	poor	4–5	4
	fair		3–4

Code: 5 — No change
4 — Slight change
3 — Moderate change
2 — Marked change
1 — Severe change

this concept, several basic substances are now available for use as gas-fading inhibitors. However, the use of inhibitors introduces a number of problems and it would be preferable if the dyestuff itself were intrinsically resistant to the action of nitrogen dioxide. Therefore, even though useful inhibitors are known, continued effort has been directed towards the synthesis of a gasfast blue anthraquinone dyestuff. Although considerable work has been done as to the mechanism of gas fading of the simpler 1-4 dialkyl amino anthraquinone dyes on secondary acetate, comparatively little attention has been paid to the mechanism responsible for the exceptionally poor light fading of these same anthraquinone dyes on the polyester fibers, such as Dacron, Kodel and Terylene. It has been postulated that the fading of anthraquinone blue dyes is an oxidation. Infra-red spectra on the photochemical decomposition products of anthraquinone blue dyes on secondary acetate have shown a change in the anthraquinone molecule itself as well as the substituents. The vulnerability of the amino or alkyl amine groups to photochemical decomposition, possibly through increased formation of peroxides, suggests that, in the case of polyester fibers, dyes of decreased reactivity to oxidative influences might be more light resistant. This working principle seems useful in that a clear correlation is established between those dyes which are poor to gas fading on acetate and those dyes which are poor to light on polyester fiber.

STRUCTURES CONTAINING ORTHO SUBSTITUENTS —— In view of the nature of the reaction causing gas fading, two fundamental concepts were used as a guiding principle in the synthesis of an anthraquinone structure which will not be destroyed by nitrogen dioxide:

1) If the 1,4-dialkylamino anthraquinone structure is retained, it should be possible to reduce the reactivity of the amino nitrogen towards an agent such as nitrogen dioxide by introducing an electronegative substituent on the anthraquinone nucleus ortho to the alkylamino group. In other words, a group such as —CN, —SO_3H, —COR, etc, in the 2 and/or the 3 position should render the amino nitrogen in position 1 and/or 4 less basic. It has been shown that there is a correlation between the degree of basicity of a dyestuff and its sensitivity towards gas fading (*3*). The less basic it is, the less it will fade.

2) Alternatively, a blue anthraquinone structure that does not contain 1,4-dialkylamino groups can be expected to be more resistant to gas fading than a structure that does contain this configuration. The problem is to obtain the desired color in the absence of the sensitive groups.

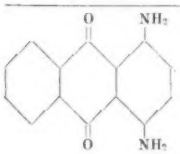
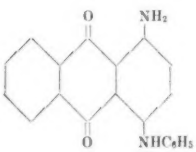
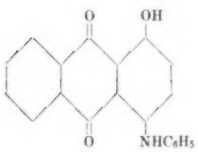
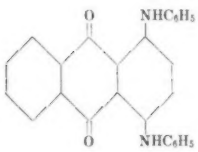
Both these approaches to the synthetic problem have been investigated. A large number of ortho-substituted derivatives have been synthesized and tested as dyestuffs. Examples of some typical structures are given in Table I. As predicted, compounds containing an electronegative group ortho to the alkylamino group are more resistant to gas fading than the corresponding unsubstituted derivatives. 1-Amino-2-cyano-4-butylamino anthraquinone fades much less than does 1-amino-4-butylamino anthraquinone (*5*). However, the degree of improvement obtained by just one ortho substituent, even one such as cyano, is not sufficient. A greater degree of improvement results when the compound contains two ortho substituents, such as in 1-amino-2,3-dicyano-4-butylamino anthraquinone (*5, 7*). Resistance to gas fading can be obtained with one cyano group by replacing the alkylamino with an arylamino group, forming a structure such as 1-amino-2-cyano-4-phenylamino anthraquinone. However, the introduction of these ortho substituents has an unfavorable effect upon the dyeing properties of the resulting compound. In general the affinity is low, the dyebath stability is poor, and the dyeing rate is slow.

The concept of diortho substitution and the use of carboxy ethanol amides has been combined by DuPont in its 1,4-diamino dicarboxy imide structures (*6*). These dyes, which give blue-green shades are, however, still of limited affinity for either polyester or acetate fibers. The structure has shown considerable increase in dyeing affinity over such dyes as 1,4-diamino-2,3-dichloro anthraquinone and 1,4-diamino-2,3-dicyano anthraquinone.

STRUCTURES CONTAINING NO AMINO OR ALKYL AMINO GROUPS —— The concept of an anthraquinone blue dye which contains no free amino or alkyl amino

TABLE II

Effect of phenylamino group in reducing gas fading

Structure	Affinity & pile-on	Gas-fading change after	
		One AATCC unit	Two AATCC units
	very good	2	1
	good	3	2
	fair	5	4-5
	poor	5	4

Code: 5 — No change
4 — Slight change
3 — Moderate change
2 — Marked change
1 — Severe change

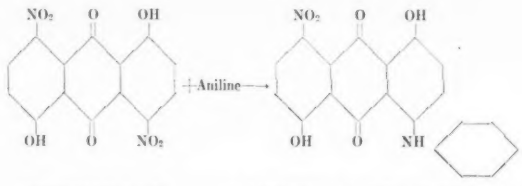
groups appears logical. 1,4-dianilino anthraquinone, although possessing limited affinity on secondary acetate, was of greatly improved resistance to gas fading as compared with the 1,4-dialkyl amino anthraquinone.

A comparison (Table II) of the gas fading of 1-amino-4-phenyl-amino anthraquinone with that of 1,4-diamino anthraquinone and of 1-amino-4-methylamino anthraquinone, shows that replacing a 1-amino or a 1-alkylamino group with an arylamino group greatly reduces the sensitivity of the molecule towards nitrogen dioxide. This effect was also evident from Table I, where 1-amino-2-cyano-4-phenylamino anthraquinone is shown to be slightly more resistant to gas fading than the corresponding butylamino derivative. If the other amino group is also replaced by a resistant group, such as a hydroxyl, a dyestuff results which shows a high level of resistance to gas fading. Acetate fabrics dyed a deep purple with 1-hydroxy-4-phenylamino anthraquinone show only a slight shade change after 4-5 units of gas fading in the AATCC test chamber.

The problem was to find structures free of amino or alkylamino groups which would meet the requirements of blue shade on the fiber and reasonable dyeing affinity. The dye 1,5-dihydroxy-4,8-dianilino anthraquinone possesses only slight affinity. The objective was met in the synthesis of the structure 1,5-dihydroxy-4-arylamino- 8-nitro-anthraquinone (*8*).

SYNTHETIC METHOD ——— These dyestuffs can be made by heating either dinitroanthrarufin or dinitroanthrachrysazin with the appropriate arylamine. Under the correct reaction conditions one, and only one, of the nitro groups is replaced by an arylamino group, yielding the desired product. (See Figure 1).

Details of the procedure have been published in the patents assigned to the authors (*8, 9*). Structural variants of this basic dye structure also have been the subject of considerable work by Eastman (*10*) dye chemists. The aromatic amine replaces the nitro group which then is evolved as an oxide of nitrogen. The evolved oxides of nitrogen diazotize the excess amine, which decomposes as the diazonium compound. At the higher temperature of the condensation, nitrogen is evolved and water is liberated. Diazo amino azo benzenes are also produced and must be removed for purposes of purity of dye.



Dinitroanthrarufin — 1,5 Dihydroxy-4-anilino-8-nitro anthraquinone

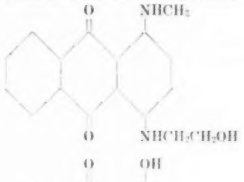
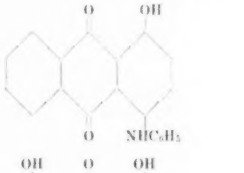
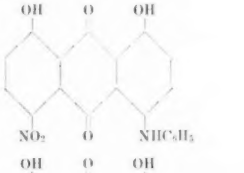
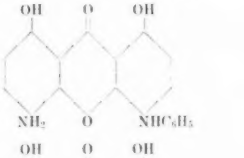
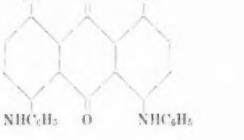
Figure 1

Process studies in our laboratories have shown that the reaction taking place in methyl cellosolve gives the most satisfactory results. The reflux temperature at 120-125°C gives condensation within the optimum range. If temperatures are permitted to rise too high, a dianilino dihydroxy anthraquinone is formed. Optimum ratios of aromatic amine are employed in order to give the best pile-on color, least artificial light change, and best colorfastness. For purest dye, the condensation is best carried out in an atmosphere of nitrogen.

PROPERTIES ON ACETATE AND POLYESTER FIBER———The bath-

TABLE III

Blue anthraquinone structures containing no free aliphatic amino group

Structure	Color	Affinity & pile-on	Gas-fading change after: One AATCC unit	Four to five AATCC units	Forty hrs light on Dacron
	blue	very good	2	0-1	1
	purple	fair	5	4	4
	blue	fair	5	4	4
	greener blue	good	3	2	2
	blue green	very poor	5	4	4

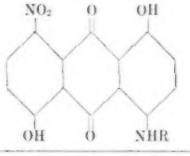
Code: 5 — No change
4 — Slight change
3 — Moderate change
2 — Marked change
1 — Severe change

ochromic effect of a nitro and an hydroxyl group in the 5 and 8 position has been found to be sufficient to convert the structures into the desired blue dyestuffs without interfering with the improved gas fastness.

Table III shows the structural relationship of the phenyl derivatives of these compound to 1-hydroxy-4-phenylamino anthraquinone and to 1-methylamino-4-hydroxyethyl-amino anthraquinone. 1, 5-Dihydroxy-4-phenylamino-8-nitro anthraquinone and 1,8-dihydroxy-4- phenylamino-5-nitro anthraquinone are both blue deystuffs for acetate which do not contain the 1, 4-dialkylamino configuration. Acetate fabric dyed with these compounds exhibits only a slight shade change after five AATCC units of gas fading. The change which takes place is on tone and does not include the reddening that has proved to be such a problem with the 1, 4-dialkylamino derivatives. The generic structure has been found to have excellent light-fastness on polyester fiber. It is clear that this original work aimed towards a structure which would be gas-fading resistant has also been useful in introducing dyes for Dacron and other polyester fibers which have met the problem of blues with good lightfastness.

TABLE IV

Dyeing and fastness properties of the 1,5-dihydroxy-4-arylamino-8-nitro anthraquinones



R =	Color	Affinity & pile-on	Gas fading Four to five AATCC units	Lightfastness change Forty hrs exposure
	reddish blue	good	4–5	4
	greenish blue	good	1–2	2
	neutral blue	good	4	3
	neutral blue	fair	1–2	4
	reddish blue	fair	4–5	4
	reddish blue	very poor	2	4
	reddish blue	poor	4	4
	greenish blue	very good	2	4
	reddish blue	very good	4–5	4
	neutral blue	fair	2	4

Code: 5 — No change
4 — Slight change
3 — Moderate change
2 — Marked change
1 — Severe change

STRUCTURE VARIATIONS——Although both these new blue structures were shown to have a high level of resistance to light and gas fading, it was found that the general dyeing properties are not optimum on acetate. Pile-on, dyebath stability, rate of dyeing and exhaustion required improvement.

With the objective of obtaining a structure with improved dyeing properties and with the same excellent resistance to gas fading shown by 1, 5-dihydroxy-4-phenylamino-8-nitro anthraquinone, a homologous series has been synthesized in which the only difference between the compounds is the nature and the position of the substituent on the arylamino radical. Such a series can be prepared by condensing the appropriate amine with dinitroanthraufin as described above. Of the dinitro dihydroxy anthraquinone isomers, the 1, 5-dihydroxy was used to establish the basic principles governing the relationships between structure, color, dyeing properties and fastness properties. In the 1, 4-dialkylamino anthraquinone series, the 1, 4-dimethylamino derivative has very poor dying properties; whereas the 1-methylamino - 4-hydroxyethyl-amino derivative has excellent dyeing properties. This suggested that introduction of hydrophilic groups might lead to structures of improved properties.

Many of the arylamines used to prepare this new series of compounds contain a free hydroxyl group, either directly on the benzene ring as in the amino phenols or on an alkyl chain as in aminobenzyl alcohol and aminophenylmethyl carbinol. These

amines can be prepared as either the para, meta, or ortho isomer so that from the condensation products with dinitroanthrarufin, it is possible to ascertain the role of the hydroxyl group in determining dyeing properties; the effect on dyestuff characteristics of whether the hydroxyl group is aliphatic or aromatic; and the changes in properties resulting from a change in the position of the substituent on the arylamino ring. Similar structures without the hydroxyl group have been synthesized for use as a point of reference. The color, the fastness properties, and the dyeing properties of all the compounds resulting from this synthetic program have been tested and evaluated by standard dyeing methods on secondary acetate. The evaluations for representative dyes were also carried out on Arnel triacetate fiber and on Dacron polyester fiber.

COLORFASTNESS AND STRUCTURE———Table IV summarizes the properties of the compounds formed by reacting aminophenols and various derivatives of aminophenol, such as anisidine, phenetidine, and 2-hydroxyphenetidine with dinitro-anthrarufin. Examination of the gas-fading characteristics of these derivatives of 1, 5-dihydroxy-4-arylamino-8-nitro anthraquinone reveals some interesting facts. The introduction of hydroxy or a methoxy group in the para position on the arylamino radical renders the molecule much more reactive towards nitrogen dioxide. Thus the analog made from p-anisidine changes more in the gas-fading chamber than does the unsubstituted parent compound, 1, 5-dihydroxy-4-phenylamino-8-nitro anthraquinone. On the other hand, the presence of a hydroxy or a methoxy group in the meta position does not have an adverse effect upon the gas-fading characteristics of the molecule. Fabrics dyed with the compound made from meta anisidine show only a slight change after exposure to five AATCC units of gas fading; whereas the para anisidine derivative changed markedly and the anilino compound very little. The relationship between the compounds containing an -OR group in the meta position and those with the same substituent in the para position remains the same whether R is hydrogen, alkyl, or hydroxyalkyl, as can be seen in Table V.

The differences observed between these two groups of compounds can be explained in terms of differences in electronic structure. The resonance structure of an aromatic compound depends upon both mesomeric and inductive effects. For example, it has been shown that an -OR group on an aromatic ring will cause an accumulation of a negative charge in the para position. In this case, this means that the electron density around the amino nitrogen is increased, rendering it more subject to attack by an electrophilic agent such as nitrogen dioxide. In contrast to this situation, an -OR substituent meta to the amino nitrogen will cause the charge to accumulate at a position adjacent to rather than on the amino nitrogen. Therefore, if anything, when there is an -OR group in the meta position, the amino nitrogen becomes slightly less susceptible to attack by an electrophilic agent than when the nitrogen atom is a part of an unsubstituted aryl-amino radical.

DYEING PROPERTIES AND STRUCTURE———The series of compounds in Table IV also reveals some interesting information about the relationship between structure and dyeing properties. A comparison of the pile-on and affinity of the derivatives made from aminophenol and from anisidine shows that the presence of a free hydroxyl group does bring about a great improvement re-

TABLE V

Dyeing and fastness properties of the 1,5-idhydroxy-4-arylamino-8-nitro anthraquinones

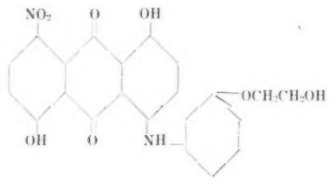
R =	*Color neutral blue*	*Acetate Affinity & pile-on*	*Gas fading Four or five AATCC units*	*Lightfastness change Forty hrs exposure*
	reddish blue	good	4–5	4
	reddish blue	fair	4	4
	reddish blue	fair	4–5	4
	greenish blue	very good	4–5	4–5
	reddish blue	very good	4–5	4–5
	reddish blue	very good	4–5	4
	greenish blue	very good	4–5	4–5
	reddish blue	very good	4–5	4
	greenish blue	fair	3–4	2
	neutral blue	fair	3–4	4

*Disclosed in Eastman patents with other hydroxy alkyl analogs

Code: 5 — No change
4 — Slight change
3 — Moderate change
2 — Marked change
1 — Severe change

gardless of whether it is in the meta or para position. This increase in affinity is probably due to increased solubilization of the dyestuff both in the aqueous dyebath and in the fiber itself. The hydroxy group functions just as well at the end of an alkyl chain as on the aromatic ring. This is shown by the excellent affinity for acetate of 1,5-dihydroxy-4-para-hydroxyethoxyphenylamino-8-nitro anthraquinone. Increasing the length of this chain by introducing several ether linkages does not increase the affinity. Evidently the increase in molecular size offsets the increased solubility due to the hydroxyl group.

There is one compound in this series that combines both of the above-mentioned structural requirements in one molecule. 1,5-Dihydroxy-4-meta-hydroxyethoxyphenylamino - 8-nitro anthraquinone



contains the -OR substituent in the meta position on the arylamino radical and it also contains a hydroxyl group on the alkyl chain of this substituent. Consequently this compound is a dyestuff with good affinity and pile-on for secondary acetate and which also exhibits a high level of both gas- and lightfastness. The relationship between lightfastness and structure has not been discussed because in general the lightfastness of these anthraquinone derivatives does not present a problem. This dyestuff is a satisfactory neutral blue with somewhat reddish tones. The fact that the color is on the reddish side is consistent with other observations in this series, because in each instance the meta isomer was found to be redder than the corresponding para isomer. Again, this difference is one that is probably related to differences in the overall electron distribution within the molecule.

Table V summarizes the properties of the compounds formed by reacting various derivatives of toluidine with dinitroanthrarufin. In this series also, better gasfastness results if the substituent on the arylamino radical is in the meta rather than the para position. A comparison of the degree of change after five AATCC units of gas fading of the meta and para toluidine analogs reveals that both compounds are very resistant to gas fading but that the meta isomer is still slightly more resistant than the para isomer.

A much greater difference is found between meta and para isomers when the substituent is an alkoxy rather than an alkyl group. The data also emphasizes the point that the initial level of gasfastness is much greater with a para-substituted derivative if the substituent is an alkyl rather than an alkoxy group. This is very obvious with the methyl compounds and assumes even more significance if the properties of the compounds made from para-hydroxyethoxy aniline and from para-hydroxyethyl aniline are compared. These two structures differ from one another by only one oxygen and yet their reactivity towards nitrogen dioxide is very different.

REACTIVITY AND ELECTRON CHARGES———The differences in gas fading observed within this group of compounds as well as those found between it and the first group can also be explained on the basis of electron configuration. The electromeric changes which occur when an aromatic ring contains an alkyl group have not been as well defined as in the case of the alkoxy group. However, although the mechanism is believed to be different, it is known that there is a slight tendency for an alkyl group to increase the negative charge in the para position. This tendency is very much less than that found with the alkoxy group, which means that the amino nitrogen para to an alkyl group does not carry nearly so heavy a negative charge as does the amino nitrogen para to an alkoxy group. Consequently, the latter is much more subject to attack by an electrophilic agent than is the former, which explains why 1,5-dihydroxy - 4 - parahydroxyethylphenylamino - 8 - nitro anthraquinone resists gas fading; whereas, 1,5-dihydroxy - 4 - parahydroxyethoxyphenylamino-8-nitro anthraquinone is very sensitive to such changes.

The relatively minor difference in the level of gas fading shown by the para toluidino analog as compared to the meta toluidino analog can also be attributed to the fact that there is only a slight tendency for an alkyl group to cause a charge to accumulate in the para position. In this instance this means that the charge on the amino nitrogen para to the alkyl group is not very much greater than the charge on the amino nitrogen meta to the alkyl group. Therefore, both nitrogens react with an electrophilic agent to about the same degree, with the amino nitrogen meta to the alkyl group being slightly more inert in this respect. This situation is quite different from that found with the alkoxy derivatives. If there is more than one substituent on the arylamino radical, the end result will depend upon the action of both groups. For example, the presence of a para methyl group in the compound made from 5-amino-2-methyl benzyl alcohol reduces the gas fading of this analog below that of the compound made from meta aminobenzyl alcohol.

DYEING PROPERTIES AND STRUCTURE———Factors which influence the dyeing properties of disperse (nonionic) dyes have been the subject of a number of recent publications (*12, 13, 14*). The principles can be applied to the range of anthraquinone blue dyes to explain the variations in dyeing properties.

DISPERSION PROPERTIES———Of first importance is the tendency toward crystallization in the dyebath. Unlike many widely used disperse dyes, the water solubility of these dyes as a group is low. Wide differences in crystallization tendency are noted in the series. In general those dyes containing alcohol groups show much less tendency towards particle size growth in the dyebath. The aniline structure shows improved dyebath stability with evidence of less filterable crystals on digestion for one hour at 95°C than the toluidino and the phenetidino homologs. Comparison with the dyes containing the solubilizing alcohol groups shows superiority of the latter structures. The tendency to crystallize will depend on the isomeric form under consideration, ie, whether it is a 1,5 or 1,8-isomer.

The mechanism of dyeing with disperse dyes involves absorption of the dye from its water solution. If water solubility is initially too low or if rate of transfer from insoluble particle to water solution is reduced because of large particle size, dyeing rate will be materially reduced. Surface dye will be noted on the fibers and if dyeing accelerant is present, the chance of dye spots will be increased.

DYEING BEHAVIOR OF ISOMERIC MIXTURES———The behavior of mixtures of isomers is of practical significance. There is a distinct difference in the extent to which the various isomers can be dispersed under standard conditions. The 1,5-dihydroxy isomer of both the analog made from para-aminophenyl ethanol

and from meta-aminobenzyl alcohol forms a very poor dispersion, even though the 1,8-dihydroxy isomer forms an excellent one. In contrast to this, it is the 1,8-dihydroxy isomer of the analog made from meta-aminophenylmethyl carbinol that has the lower degree of dispersibility.

Another way in which the isomers of the various analogs differ is in their sensitivity to the pH of the dyebath. For each isomer there is a pH above which it cannot be used because of lack of affinity due to formation of alkaline salt and, except for the 1,8-dihydroxy isomer of the para-aminophenyl ethanol analog, there is a pH below which it cannot be used because of precipitation. This means that, for the most part, the pH of a dyebath containing these compounds has to be kept within a rather narrow range. This problem can be readily solved for the meta-aminophenylmethyl carbinol analog by combining the two isomers into one dyestuff mixture. Apparently the presence of both isomers reduces the tendency towards cyrstallization of either isomer and a dyestuff results which will readily disperse and form a stable dyebath giving heavy shades over a wide pH range. This may be due to formation of mixed melting point that reduces crystallization rate. The ratio of isomers that will produce these results varies from 25 parts of one and 75 parts of the other to just the reverse. The use of dyestuff mixtures rather than pure compounds in order to improve dyeing properties is well known in the patent literature and in practice, so it could be expected that isomeric mixtures of the other two analogs would behave similarly. They do show the same effect but not to the same degree. The extent of improvement in the dyeing properties of the other two analogs is not as great and the resulting dyestuffs are not quite as satisfactory as that of m-amino phenyl methyl carbinol (Table VI).

SPECIFICITY OF DYE FOR ACETATE OR POLYESTER FIBER—— The dyeing rates of all these colorfast anthraquinone dyes are typical of the slow-dyeing types, which require higher temperatures and which diffuse into the fiber at slower rates. Microscopic cross sections show ring dyeing in initial stage of dyeing. The comparative dye pickup on secondary acetate, Arnel triacetate, and on Dacron as carried out in representative dyeings, demonstrates the phenomenon of intrinsic affinity of dye for fiber and specificity of dye for the fiber.

In Table VII, the anilino structure is directly compared with the m-amino phenyl methyl carbinol structure under various dyeing conditions. The exhaustion of these dyes on secondary acetate parallels that on triacetate using conditions where dyeing rates are equalized by variations in temperature. In these cases, as well as in comparisons on a larger group, no specificity of dye was shown for one acetate fiber over the other.

However, in the case of polyester fiber, specificity was clearly shown. This is true whether dyeings are carried out in separate dyebaths or in dyebaths where both fibers are present for competitive distribution. The greater substantivity of the anilino dye for Dacron is of increased significance since Arnel is generally considered to be more readily dyeable. A methyl salicylate-based carrier was used. Similar results are obtained using ortho phenyl phenol carrier. Conversely, the m-amino phenyl carbinol structure shows preference for the Arnel. The specificity of dyes for polyester fibers has been noted by Schroeder (*17*), who points out that dyes containing a minimum of hydrophilic groups tend to give better exhaustion on Dacron.

The differences also follow deter-

TABLE VI

Effect of isomerism upon dyeing properties of the dihydroxy-4-arylamino nitro anthraquinones

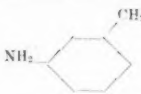
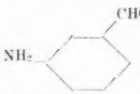
Analog	*Isomer*	*Affinity at 1% level*
Aniline	1,5-dihydroxy	good
	1,8-dihydroxy	fair
m-aminobenzyl alcohol	1,5-dihydroxy	poor
	1,8-dihydroxy	very good
p-aminophenyl ethanol	1,5-dihydroxy	poor
	1,8-dihydroxy	very good
m-aminophenylmethyl carbinol	1,5-dihydroxy	very good
	1,8-dihydroxy	poor

TABLE VII

Specificity of dye for fiber relative color value——visual

Fiber	*Anilino structure*	*m-Amino phenyl methyl carbinol*
Acetate Two hours at 80°C	70	100
Triacetate Three hours at 95°C	60	75
Triacetate Two hours at 95°C 10% methyl salicylate carrier	70	95
Triacetate One hour at 126°C. 20 pounds pressure	75	105
Dacron Two hours at 95°C. 10% methyl salicylate	120	80
Dacron One hour at 126°C. 20 pounds pressure	110	85
Dacron and Arnel Two hours at 95°C and carrier	120—Dacron 65—Arnel	110—Arnel 60—Dacron
Dacron and Arnel One hour at 126°C. 20 pounds pressure	130—Dacron 55—Arnel	95—Arnel 80—Dacron

mination of intrinsic solubility in the fiber. When dyeings are carried out on triacetate using excess dye and for periods of 48 hours, to note limits of solubility in the fiber, the amino phenyl methyl carbinol dye shows greater pickup on the Arnel than on the anilino dye. If outer layer of fiber is initially saturated with dye, the rate-determining step will be the rate of inward diffusion. Dyeing rates must then be considered as dependent on both factors of intrinsic solubility within fiber and rate of inward diffusion which is characteristic of the dye molecule and its kinetic behavior.

SUMMARY

A series of blue anthraquinone dyes synthesized by condensation of aromatic amines with dinitro anthrarufin, dinitro chrysazin or their mixtures have been evaluated as to colorfastness and dyeing properties. Variations in structure have been related to these properties.

Resistance to gas-fading change on acetate fibers is shown as characteristic of dyes which do not contain vulnerable aliphatic amino groups.

Correlation is shown in this series between structures which are resistant to gas fading and those which show good lightfastness on polyester fiber.

Dyeing specificity is shown between polyester fiber and acetate fiber, with more hydrophobic structure showing better affinity for polyester fiber.

The use of isomeric mixtures of dyes is shown to give increased dyebath stability and higher exhaustion.

Dyeing properties are related to basic principles of particle size in dyebath, solubility of dye in water phase, and diffusion rate into specfic fiber.

ACKNOWLEDGMENT

The authors wish to thank the Celanese Corporation of America for permission to publish the data herein and both Reiner G Stoll, director of applications and product development, and Fred Fortess, manager of Dyeing and Finishing Laboratories, for their interest and encouragement in publication of this paper, which combines basic study of dye structure with practical applications to dyeing phenomena.

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Part II—Diphenylamine Yellows

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Celanese Corp of America

The relation of structure to dyeing properties has been studied in a wide range of lightfast diphenylamine yellow dyes synthesized for the purpose. These materials were made by variation of the substituents placed on a p-sulfonamide grouping of 2-nitrodiphenylamine-4-sulfonamide.

The effects of both increased molecular weight and of decreased hydrophobicity (contributed by oxygenated groups) on dyeing properties were determined. The evaluation of the twenty-eight dyes presents data, which confirm principles established for dyeing behavior of useful disperse dyes: a) intrinsic solubility within the fiber, b) good dyebath dispersion, c) balanced water solubility, and d) satisfactory rate of diffusion within the fiber.

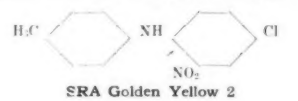
Where increase in molecular weight is obtained by hydrophobic groups only, the dye of best properties is obtained by use of an aromatic substituent on amide groupings. Thus a dye showing high washfastness on acetate and Arnel is 2-nitrodiphenylamine-4-sulfanilide.

A balanced combination of decreased hydrophobicity derived from presence of hydroxyl groups and increase in molecular weight by aliphatic groups has been established as a principle for obtaining yellow dyes which combine satisfactory dyeing properties and pile-on with good wetfastness.

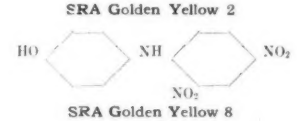
INTRODUCTION

The yellow nitrodiphenylamines are the most important members of the dye group in which the nitro group constitutes the chromophore.

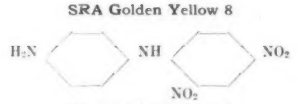
Nitrodiphenylamines have long been used for coloring wool and leather in yellow shades as represented by Amido Yellow E. Several of the early disperse dyes of this series used for coloring acetate fiber were simple derivatives of o-nitrodiphenylamine. The azo dyes possess greater tinctorial value. However, their deficiencies in lightfastness and in phototropism limit their use. Examples of such disperse dyes are:



SRA Golden Yellow 2



SRA Golden Yellow 8



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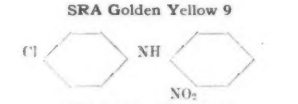
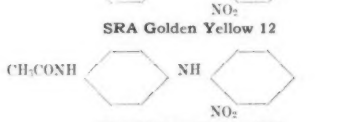


SRA Golden Yellow 12



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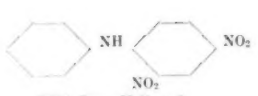
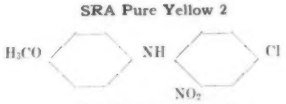


SRA Pure Yellow 2



SRA Golden Orange 3

These dyes have excellent fastness to light with the exceptions of SRA Golden Yellows 8 and 9, and SRA Pure Yellow 2. The presence of a p-nitro group in the molecule consistently gives poor lightfastness, whereas compounds with o-nitro groups have good lightfastness.

The simple diphenylamines do not have ideal dyeing properties. It is difficult to prepare good disperse powders which will give stable dyebath dispersions and certain of them have a strong tendency for crystallization in the dyebath with consequent reduction in affinity. In this respect, their behavior parallels that of the anthraquinone blues discussed in Part I. Moreover, their low molecular weights make them poor with respect to both sublimation and washfastness.

Variations in the structure have

been used to improve these deficiencies. Thus orthonitro diphenylamine dyes have been reported in which the para position is occupied by the cyano, sulfone, carboxy amide or carboxyester groups. However, it was not until compounds with the sulfonamide group (SO_2NH_2) in the para position were prepared that structures having better dye dispersibility than the previous SRA colors were available. The simplest member of this group is the 2-nitrodiphenylamine-4-sulfonamide first synthesized by Fischer (*1*). This structure has been used by Eastman (*2*) for a group of dyes having no substitutions in the sulfonamide portion of the molecule. These dyes, which showed excellent lightfastness but had poor washfastness, are designated in the new *Colour Index* as Disperse Yellows 33-34.

The simple sulfonamide yellow possesses the property of reverse affinity at high dyeing temperature as shown by its lower exhaustion at high dyeing temperature of 90°C as compared to 60°C.

The advent of Arnel cellulose triacetate emphasized the need for a yellow of good washfastness, dyebath dispersibility, and good lightfastness. Of additional importance was the need for a yellow which would have balanced dyeing rates with the reds and blues.

The need for a yellow on Dacron is not as great as that for blues of good lightfastness. Celanthrene Fast yellow GL (CI Disperse Yellow 2) is a nitroacridone and thus is essentially a diphenylamine dye in its structure. The azo dye represented by prototypes of Celliton Yellow 4RL (CI Disperse Yellow 23) shows greater staining on wool. The high temperature behavior of the simple sulfonamide yellow gives reduced affinity at the higher temperatures used for the dyeing of polyester fiber.

In view of the deficiencies of the simple sulfonamide dye with respect to fastness to washing and to balanced dyeing properties, the authors undertook the synthesis of dyes with the following variations in structure and examined the dyeing properties. It was thought that a) an increase in molecular weight and b) that the incorporation of oxygenated groups would decrease the sublimation and improve fastness to washing, while yielding dyes having good affinity and dispersion properties as well as balanced dyeing rates.

Such variations included:

1) Substituents on the amide nitrogen, such as 1 or 2 alkyl groups,

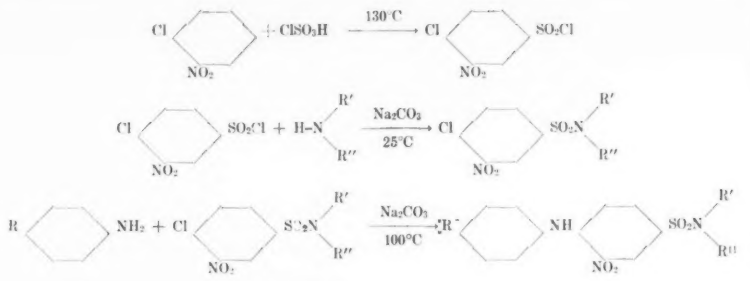
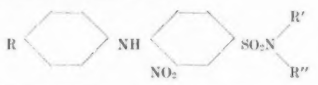


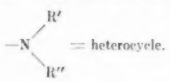
Figure 1

an alicyclic grouping, aromatic substitution, or a heterocyclic substituent.

2) Substituents in the R position, such as alkyl, alkoxyl, aryl, halogen, and acylamino groups,



in which **R** = alkoxyl, alkyl, aryl, halogeno, acylamino; **R′** or **R″** = **H**, alkyl, aryl, alicyclic; and



EXPERIMENTAL AND DISCUSSION

SYNTHETIC PROCEDURES —— The synthetic route used involved a two-step condensation, in which 4 - chloro - 3 - nitrobenzenesulfonyl chloride (*3*) was first reacted with an amine to form a sulfonamide, which was in turn condensed with an aromatic amine to produce the diphenylamine dye shown in Figure 1.

By means of this synthetic route, the dyestuff structures described in Tables I and II were prepared. Variations in molecular weight, together with the use of aliphatic, aromatic and alicyclic groups as well as oxygenated substituents, resulted in a series of dyes for which correlations between structure, color, dyeing properties and washfastness could be elucidated.

STRUCTURE AND DYEING PROPERTIES——The dyeing properties of representative members of the series of diphenylamine sulfonamides are tabulated in the tables, which show dyeing rate, crystallization tendency, washfastness, and percent of dye lost in washing.

Dyeings were carried out on secondary acetate at 80°C for one hour using 1% of pure dyestuff based on fabric weight in a liquor-fabric ratio of 50:1. After the surface dye was rinsed off and the fabric conditioned, a weighed portion was dissolved in acetone and the pickup of dye determined by spectrophotometric measurement.

Dyeing rates were determined by removing samples at 20 and 40 minutes and noting the build-up of shade.

The aggregation tendency of the dye was ascertained by heating the dyebath at 80°C for two hours and filtering in order to observe any crystallization or aggregation of the dye, bringing about the formation of large particles in the dyebath.

The washfastness of the dyes was obtained by washing the dyed fabric in a Launder-Ometer for 30 minutes at 120°F, in the presence of five g/l of soap, or for 45 minutes at 160°F in presence of soap and soda ash (#3 AATCC Test) with spectrophotometric measurement of the color lost from the dyed fabric.

The following observations are made with respect to the relation between structure and dyeing properties listed in Table I.

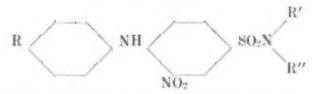
The limiting factors in dyeing are the intrinsic affinity of the dye for the fiber, the crystallization tendency, the solubility of the dye in water, and the diffusion rate of the dye into the fiber (*5, 6*).

Prolonged dyeing times, such as six hours, with excess concentrations of dye may be used to establish the intrinsic affinity or saturation value of the dye for the fiber. Among disperse dyes, the solubility of the dye within the fiber ranges from 0.2% to 14% on the weight of the fiber. Thus, the compound represented by Structure #6 shows low solubility in the fiber (0.85%), whereas Structure #5 has a saturation capacity of 8.4%.

The mechanism of dyeing with disperse dyes involves absorption of the dye from its aqueous solution. The rate of dyeing would be dependent on the water solubility of the dye. Bird, et al (*5*) have measured the water solubility of a number of dis-

TABLE I

Dyeing properties of diphenylamine yellow dyes



Structure	Grouping on R	R′	R″	Dyeing rate	Crystallization tendency	120°F AATCC Test: Wash fastness	120°F AATCC Test: % Loss on washing
1	H	H	H	rapid	none	low	29
2	H	H	$-CH_2CH_2OH$	rapid	none	low	26
3	H	C_2H_5	C_2H_5	moderate	slight	moderate	19
4	H	H	cyclohexyl	fairly slow	moderate	moderate	15
5	H	H	C_6H_5	slow	moderate	high	8
6	H	H	3,5,5-trimethylhexyl	very slow	appreciable	high	12
7	H	$-CH_2CH_2OH$	C_6H_5	slow	moderate	very high	6
8	OCH_3	H	C_6H_5	very slow	appreciable	very high	6
9	OCH_3	H	H	rapid	none	low	26
10	OCH_3	H	$CH_2CHOHCH_3$	fairly slow	none	moderate	12
11	C_6H_5	H	H	moderate	appreciable	low	26
12	H	H	morpholine	moderate	slight	moderate	16

perse dyes and found it to vary from 0.2 mg to 108 mg per liter at 80°C. Structure #1 has very high solubility in water, whereas Structure #7 has only moderate solubility. The formation of larger crystalline particles in dyebath digestion further reduces the availability of dye in the water phase.

Hydroxyl groups in the molecule tend to increase the water solubility. A combination of hydroxyl groups with increased molecular weight in Structures #7 and #10 leads to dyes having good dyeing rate, as well as higher washfastness. Where arylamine substituents, such as toluidine or anisidine, were used, dispersibility was poor and dyes were not further examined.

The data illustrate the correlation found between dyeing rate and fastness to washing. The rate of diffusion of the dye out of the fabric during washing parallels the rate of absorption of the dye from the dyebath. Thus those dyes which are quickly taken up are those most readily lost in washing *(8)*.

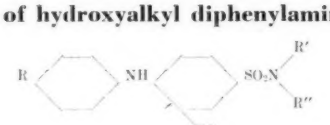
The increase in molecular weight is not the sole determining factor in the dyeing rate. Thus the compounds represented by Structures #5 and #11 have the same molecular weight, while dyeing rates and washfastness are entirely different. The substitution of $CH_2CHOHCH_3$ for CH_2CH_2-OH does give a pronounced difference in dyeing rate. Here the diffusion rate within the fiber may well be the controlling factor, as shown by cross sections of the dyed fiber in the initial part of the dyeing cycle. Dye Structures #5 and #10 have shown sufficiently balanced properties, including good exhaustion in higher dyeing concentrations, to warrant their use as commercial dyes. As a direct result of this work, Structure #5 is now established as a commercially offered dye that meets the need for a yellow dye of good light- and wetfastness on acetate and on Arnel. The dye is also finding use on polyester fibers.

HYDROXY ALKYL DIPHENYLAMINE YELLOWS —— Table II shows the properties of a series of hydroxy alkyl diphenylamine yellows. Structural variation in this group has been directed towards the objective of obtaining that balance of molecular weight and hydroxyl content that would give the optimum with respect to dyebath stability, dyeing rate, pile-on and the desired high level of washfastness. Several of the hydroxy alkyl diphenylamine yellows have been disclosed in the broad claims of an Eastman patent *(7)*. These were synthesized in this work to obtain a range of structures for critical evaluation of structure versus dyeing properties.

Of the 17 hydroxy alkyl diphenylamine yellow dyestuffs synthesized, those with melting points below 100°C were eliminated from further consideration because of the tendency for such dyestuffs to separate as oils in the dyebath and thus give spotty dyeings. For this reason, the dyestuffs 4′-ethoxy-2-nitrodiphenylamine-4-sulfon-hydroxy-tertiary butylamide, 2-nitrodiphenylamine-4-sulfon-α-α-dimethyl-β-hydroxypro-

TABLE II

Properties of hydroxyalkyl diphenylamine yellows



Structure	Groupings on R	R′	R″	Optical Densities: 1% dyeing	2% dyeing	3% dyeing	Pile-on (Ratio of optical densities of 1% & 3% dyeings	Crystallization	% Dye lost at 160°F #3 AATCC wash test
1	H	H	C_2H_5	089	169	193	2.17	slight	34.0
2	H	H	$-CH_2CHOHCH_3$	075	132	188	2.51	none	49.3
3	OC_2H_5	H	$-CH_2CHOHCH_3$	101	175	244	2.42	none	41.5
4	H	H	$-C(CH_3)CH_2OH$	080	146	200	2.50	none	40.0
5	OC_2H_5	H	$-CH(CH_3)CHOHCH_3$	103	194	272	2.64	none	37.8
6	H	H	$-CH(CH_3)CH_2CH_3$	086	156	225	2.62	none	36.0
7	OC_2H_5	H	$-CH(CH_2OH)CH_2CH_3$	105	202	272	2.59	slight	31.0
8	H	C_2H_5	$-CH(CH_2OH)_2$	091	164	232	2.55	none	41.0
9	H	$-CH_2CHOHCH_3$	$-CH_2CHOHCH_3$	060	085	089	1.48	good	....
10	H	$-CH_2CH_2OH$	$-C_2H_5$	085	140	148	1.74	moderate	23.5

pylamide and 4′-ethoxy-2-nitrodiphenylamine-4-sulfon-(N-ethyl-N-β-hydroxyethyl) amide were removed from the list of dyestuffs to be further evaluated.

Certain of these yellow dyestuffs tended to crystallize from the dyebath when used as oil colors, but since none of them crystallized to a greater extent than 2-nitrodiphenylamine-4-sulfonanilide does, this disadvantage was not used as a criterion for elimination of dyestuffs from consideration. Disperse powders are often observed to give less crystallization than oil colors dyed via solvent dispersion.

Those dyestuffs which did not show good affinity by visual examination were also removed from the list of eligible dyestuffs. These included 4′-ethoxy-2-nitro-diphenylamine-4-sulfon-β-hydroxyethylamide, 2-nitrodiphenylamine-4-sulfon-bis-β-hydroxyethylamide and its 4′-ethoxy analog and 4′-ethoxy-2-nitrodiphenylamine-4-sulfon-bis-β-hydroxypropylamide.

The dyeing properties of the various hydroxyalkyl diphenylamine yellows are directly compared in Table II. The addition of a hydroxyalkyl group in Structure #10 has not improved the dyeing rate or exhaustion of this dye over that of Structure #1. An increase in the tendency for crystallization was noted. The washfastness was materially raised. In this group, desorption was carried out at higher wash temperatures corresponding to the 160°F AATCC wash test. The desorption results are an indication of the diffusion properties of the dyes.

The optical densities show the relative increase in depth of shade in a comparison of dyeings of 1, 2 and 3% of oil color at 80° C for two hours at a liquor ratio of 50-1. These dyeings were carried out in the presence of one g/l of soap on secondary acetate. Structure #9, which contains two hydroxypropyl groups, shows poorer exhaustion than the corresponding dye with only one of these hydrophilic groups.

A good balance of dyeing properties together with the retention of higher washfastness is shown by Structures #5, #6, and #7. These represent structures which combine good wetfastness with satisfactory dyeing rate and exhaustion.

RELATIONSHIP OF STRUCTURE TO COLOR———Variation of the substituents in either ring of the basic diphenylamine structure or in the sulfonamide portion of the molecule leads only to varying shades of yellow, the color throw never being sufficient to produce scarlets or reds. Redder shades of yellow, however, represented in Table III by 2R, 3R, 5R, etc, result from the use of such substituents as methyl, alkoxyl, hydroxyl, acetamino, or amino in the R position of the structural formula. The most satisfactory orange yellow dyes of this series are those containing an alkoxyl group in the 4′ or R position.

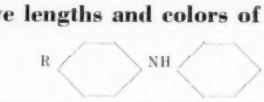
Variation of the amine used in the sulfonamide portion of the molecule fails to produce any visible change in the color of the dye, nor does the sulfonamide group itself have any effect. This portion of the structure obviously does not function as part of the chromophore. Study of the color variation in these dyes has been made both visually and spectrophotometrically. Actually, the visible change is more easily recognizable because of the lack of a sharp peak in the spectrophotometric curve.

CHARACTERIZATION OF DYES ———Much of the theory of dyeing of disperse dyes is derived from the behavior of dyes of rapid diffusion, high dyeing rates and excellent dyebath dispersibility. The examination of dyes of relatively poor solubility in the dyebath, slow diffusing properties, and slow dyeing rate presents additional information. The diphenylamine yellow, 2-nitrodiphenylamine-4-sulfanilide is of the latter type. The characterization of its dyeing properties is pertinent to basic principles of disperse dye behavior as related to a specific structure. It is of interest to both dye chemist and the practical dyer. The following characterization, as summarized in Table IV, illustrates the usefulness of such data to both the organic dye chemist and the practical dyer. (Table II).

1) *Saturation value.* The solubility in the fiber is 8.4% on fiber weight. This shows that the dye can build up in depth if given sufficient time and temperature. With the yellow of low saturation value characteristic of a long-chain nonamide ($-SO_2-NHC_9H_9$) structure the failure

TABLE III

Dominant wave lengths and colors of diphenylamine yellows



Groupings on			Dominant wave length	
R	R′	R″	m	Color
H	H	H	574	neutral yellow
CH_3	H	H	578	2R
OC_2H_5	H	H	580	4R
OCH_3	H	H	579	3R
OH	H	H	578	3R
Cl	H	H	574	neutral yellow
NH_2	H	H	584	5R
$NHCOCH_3$	H	H	579	3R
H	H	CH_2CH_2OH	574	neutral yellow
H	C_2H_5	C_2H_5	574	neutral yellow
H	H	C_2H_5	574	neutral yellow
H	CH_2CH_2OH	C_2H_5	574	neutral yellow
OCH_3	H	C_2H_5	580	4R
OCH_3	H	$CH_2CHOHCH_3$	580	4R

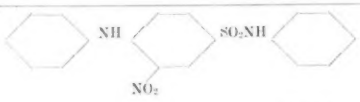
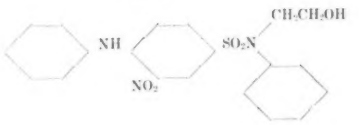
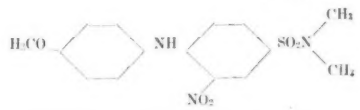
TABLE IV

Characterization of dyes on acetate

Dye	2-nitrodiphenylamine-4-sulfanilide	2-nitrodiphenylamine-4-sulfonamide
Saturation value	8.4	6.7
Solubility in water 80°C	4.0 mg/l	56 mg/
Temperature vs exhaustion (1%)		
One hour at 60°C	26	91
One hour at 80°C	81	87
One hour at 90°C	93	78
Pile on — 1 and 3% —80°C		
Ratio of optical densities two hr	1.94	2.26
Ratio of optical densities six hr	2.46	2.30
Penetration — cross section	ring dyeing	complete
Liquor ratio effect 80°C		
Exhaustion 50-1	81	87
Exhaustion 100-1	79	74
Detergent effect 50-1 LR		
Exhaustion one g/l soap	80	87
Exhaustion five g/l soap	77	66
Desorption #3 AATCC wash test % loss 1% dyeing at 70°C	34	55

TABLE V

Relative affinity for Arnel and Dacron dyed at 95°C for two hours with methyl salicylate carrier

Analog		Dacron	Arnel
I		70	100
II		55	100
III		90	100

to build up in depth was characteristic of the dye rather than the dyeing kinetics.

2) *Solubility in water.* The dye shows a limited solubility in water at 80°C, approximately from four mg/liter. Its solubility in water is only slightly increased by the addition of solubilizing surfactant, such as soap. This will influence exhaustion as function of liquor ratio and detergent.
3) *Dyeing rate as function of temperature.* The dye is of high temperature type as shown by percent exhaustion, after one hour, 40-1 liquor ratio, of 26% at 60°C, 81% at 80°C and 93% at 90°C. This factor is responsibile for good washfastness.
4) *Pile-on.* The ratio of optical densities as given in Table II for 1-2-3% dyeings (100% basis) shows steady increase in depth. This is to be expected from its saturation value. However, build up will increase with longer dyeing times (eight and 16 hours) indicative of slow diffusion into fiber and need for transfer of dye from outer ring to center of fiber.
5) *Cross section.* One hour dyeings at 80°C show outer dyed ring indicative of slow diffusion rate.
6) *Effect of liquor ratio.* The dye shows some decrease in exhaustion at higher liquor ratios of 100:1. However, this decrease is not as marked as that of the more water-soluble dye, 2-nitrodiphenylamine - 4-sulfonamide.
7) *Effect of surfactant.* The dye shows only moderate decrease in exhaustion when dyed in presence of high concentration of surfactant (five g/l soap). This decrease is less pronounced than for 2-nitrodiphenylamine-4-sulfonamide.
8) *Effect of dyeing temperature on exhaustion.* The limited water solubility at 95°C counteracts drop in exhaustion at high temperature noted for a number of disperse dyes. In a two-hour dyeing when practical exhaustion is obtained for 1% dyeing, higher value is obtained at 90°C. However, the more water-soluble 2-nitrodiphenylamine-4-sulfonamide exhibits lower value of 78% at 90°C and 90% at 60°C.
9) *The percent dye lost in desorption is also indicative of diffusion rate as related to both the dye and the fiber.* Thus, the sulfanilide structure shows less desorption, which correlates with its slower dyeing rate. On Arnel, the desorption value at 160°F (#3 AATCC test) shows loss of only 8% dye.

SPECIFICITY FOR FIBERS——The specificity of disperse dyes for Arnel and Dacron has been shown in diverse structures. In the anthraquinone blue dyes of Part I, the hydroxylalkylaniline homologs possess greater affinity for Arnel in comparative dyeings with Dacron, whereas the simple aniline dye favors the polyester fiber. Other examples of dyes which show better affinity for Dacron are the anthraquinone reds: Latyl Red B and Resoline Red BL. The variation in structure of the diphenylamine yellows afforded an opportunity to test representative dyes having varying hydrophobicity. Dyeing was carried out in separate dyebaths at 95°C for two hours using methyl-salicylate-based carrier on Arnel and on Dacron. The results based on visual estimates of depth indicate that the more hydrophobic structures tend to give better dyeing properties on the polyester fiber (Table V). Thus the phenyl ethanol dye (Analog II) shows more difference in relative depth than the phenyl (Analog I). The dimethyl amide dye (Analog III), a highly hydrophobic dye, shows the relative affinity for triacetate and polyester to be close.

SUMMARY

The relation of structure to dyeing properties has been studied in a wide range of lightfast diphenylamine yellow dyes synthesized for the purpose. These materials were made by variation of the substituents placed on a p-sulfonamide grouping of 2-nitrodiphenylamine - 4-sulfonamide.

The effects of both increased molecular weight and of decreased hydrophobicity (contributed by oxygenated groups) on dyeing properties were determined. The evaluation of the twenty-eight dyes presents data which confirm principles established for dyeing behavior of useful disperse dyes: a) intrinsic solubility within the fiber, b) good dyebath dispersion, c) balanced water solubility, and d) satisfactory rate of diffusion within the fiber.

Where increase in molecular weight is obtained by hydrophobic groups only, the dye of best properties is obtained by use of an aromatic substituent on amide groupings. Thus a dye showing high washfastness on acetate and Arnel is 2-nitro diphenylamine-4-sulfanilide.

A balanced combination of decreased hydrophobicity derived from presence of hydroxyl groups and increase in molecular weight by aliphatic groups has been established as a principle for obtaining yellow dyes which combine satisfactory dyeing properties and pile-on with good wetfastness.

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Piedmont Section———

KNIT GOODS OF ORLON ACRYLIC FIBER— PROCESSING AND DYEING*

G ROBERT TURNER
E I duPont de Nemours & Co, Inc

A general discussion of the physical handling of knit goods made of Orlon acrylic fiber and Orlon blends is given, with particular emphasis on the prevention of wrinkle marks.

Dye selection is brought up to date, with cationic dyes being grouped into slow, medium- and fast-dyeing categories. Details refer to the variables encountered in setting up a dyeing procedure and selecting dyes to produce various shades. The basic principles involved with these variables are discussed.

Particular emphasis is placed on following a specific procedure with special consideration on proper dye selection for any given shade.

INTRODUCTION

ASSUMING a fabric has the required utility, what makes it sell?

I imagine you would say either hand or color, or both. These are the factors which appeal to the ultimate customer, and in most cases they probably are decisive as to which item is selected.

The fiber under discussion today can provide the qualities you want to put into a fabric. From a very fine, cashmere-like hand, to a course, rough hand, you can have your choice. Dyes now available for dyeing Orlon acrylic fiber can provide any effect that you wish, from the very brightest of shades, to the lightest, with fully adequate lightfastness of up to 100 hours or more.

By blending Orlon with other fibers, one can obtain almost a limitless range of styling and physical properties. The fact that Orlon dyes with a class of colors not having affinity for most other fibers certainly contributes to its versatility when used in blends.

I would ask you to keep the factors of color and hand in mind throughout our discussion.

A lot has been written about Orlon in recent years; however, with regard to dyeing, the constantly increasing number of dyes available for use in coloring this fiber makes it desirable to keep up-to-date continuously.

As most of us know, the main outlets of knit goods made of Orlon are sweaters and jersey. More recently, this fiber has found extensive use in men's hosiery.

Numerous variations of Orlon and its blends are on the market today, and styling runs all the way from fine gauge work up to very bulky constructions. Mixtures of regular and high shrinkage fiber are used in varying percentages to produce a variety of effects.

* Presented April 11, 1959 at a meeting of the Piedmont Section held at the Robert E Lee Hotel, Winston-Salem, NC

DISCUSSION

CONSIDERATION OF PHYSICAL CHARACTERISTICS ——— When dyeing and finishing knit goods of Orlon, we must be fully conscious of the physical characteristics of the fiber. This is most important in order to develop the so-called "hand."

Since Orlon is thermoplastic, it becomes somewhat soft when in a hot condition, let's say above 180°F. It is, therefore, important that certain basic practices be followed when the fiber is in this state.

After any high-temperature treatment of Orlon, it is desirable to cool the bath slowly, in order to prevent the formation of wrinkles. This is most easily handled by allowing the bath to cool by radiation to about 170°F, and then by the very slow addition of cold water, until the bath is cool. Naturally, some styles require more care than others, a finer construction being more susceptible to wrinkles than a course one.

Many times, even with the utmost care, wrinkles do show up. A slow, rather heavy steaming treatment, with the fabric under some light tension, will usually remove them. If this is not satisfactory, the next best thing to do is to place the fabric back in the bath, reheat to a boil, then cool back slowly again.

This cooling procedure applies after any hot treatment of Orlon acrylic fiber, either 100% or the high percentage blends.

EQUIPMENT ——— Knit jersey material is handled quite easily on reel dyeing machines and on conventional drying, calendering and steaming equipment. Caution should be used so as not to overdry the fabric.

Dyeing of sweater bodies or strips is carried out by placing the goods in mesh bags and then dyeing in either a rotary- or paddle-type hosiery machine. Care in loading the bags is important, with about 17 to 20 lbs of strips or nine to 12 lbs of sweater bodies being placed in a 30″ by 54″ bag. About half of these poundages can be placed in a 24″ by 30″ bag. This method of loading allows freedom of movement for bulking and uniformity of dyeing, but keeps the goods firm enough so that excess tangling does not occur. Bags constructed of filament Dacron polyester fiber seem to be the most serviceable.

Hosiery, either 100% or blends, is dyed in either a paddle or a rotary machine. Here again, the goods may be placed in bags if desired.

After dyeing, slow cooling, and application of softener, one extracts the hose and places it in a tumble dryer. Drying is carried out to a point where the hose are just slightly damp. Boarding is then done on fairly cool boards at about 250°F or less. It is usually unnecessary to preboard hose constructed of Orlon acrylic fiber, although this may aid appearance in some instances.

DYES AND AUXILIARIES ——— The two general classes of dyes used for coloring Orlon are disperse and cationic or basic dyes. In general, the disperse dyes must be confined to light shades; however, the cationic dyes can be applied over the full shade range.

With either class of dyes, it is desirable to prescour the goods. A nonionic surfactant, such as Alkanol HCS, is the preferred scouring agent, although anionic types, such as Duponol RA (a fortified ether-alcohol sulfate) can be used if the goods are to be dyed with disperse dyes. If ca-

tionic dyes are to be used, it is most important to use the nonionic type, since this precludes the carry over of any anionic material into the dyebath. This is a most important factor when dyeing with cationic dyes since precipitation of the dye and any anionic surfactant present can occur.

The addition of a mild alkali, such as tetrasodium pyrophosphate, is helpful in obtaining a good prescour. Treatment can be carried out for 20 to 30 minutes at 160°F or higher, depending upon the condition of the goods.

DYEING WITH DISPERSE DYES ——— Dyeing of Orlon acrylic fiber with disperse dyes is fairly straightforward, the only real problem likely to be encountered being dye pigment agglomeration due to prolonged treatment at high temperatures. For this reason it is desirable to use a good dispersing agent, such as Alkanol HCS, in the dyebath. We would suggest 1/2 to 1% based on fiber weight, depending upon the depth of shade.

As we said earlier, disperse dyes must be confined to pastel and very light shades because of the limited buildup properties of these dyes on Orlon.

The disperse dyes, when properly selected and applied, are characterized by very good lightfastness and good washfastness. If other fibers are present in the dyebath, staining of these fibers may be a problem, so one must take care when considering the use of these dyes.

Disperse dyes for use in this case may be selected from the following:

CI Disperse Red 1
CI Disperse Red 11
CI Disperse Orange 3
CI Disperse Yellow 3
CI Disperse Blue 1
CI Disperse Blue 3
CI Disperse Violet 4
Celanthrene Brilliant Blue FRN
Latyl Yellow YL
Latyl Yellow 3G
Latyl Cerise B

DYEING WITH CATIONIC DYES ——— Most fabrics of Orlon acrylic fiber are dyed with cationic (or basic) dyes. These dyes can be applied from the lightest to the heaviest shades. A brightness unique in the dyeing field can be produced.

Table I illustrates, in three separate groups, typical basic dyes available for the dyeing of Orlon. Group I shows dyes preferred for light shades; Group II, those for medium shades; and Group III, those for heavy shades. These dyes, in general, possess excellent wetfastness, and lightfastness ranging all the way from fair up to some of the fastest known dyes of any dye class. It is fortunate that there are many dyes in this very-fast-to-light category, and thus the dyer has available the means of producing many desired shades, with outstanding lightfastness. This, together with brightness of color and sunlight durability of Orlon, suggest a variety of sportswear and utility outlets for the textile stylist.

In order to produce a saleable piece of goods, of course, one must apply the dye uniformly and evenly to the fabric. Uniformity and consistency of dyeing are perhaps the two things with which the dyer is most concerned.

To control the dyeing most effectively when using cationic dyes, one should keep the time cycle and dyeing temperature as constant as possible for any given shade.

To achieve this, it is important that dyeing should be carried out as close to 212°F as possible. After obtaining maximum temperature conditions, the rest of the dyebath system can be adjusted. Let me repeat, obtain the highest possible temperature and use this as the standard. Since Orlon acrylic fiber requires very high temperatures for maximum dyeing rate, it will be to one's advantage in the long run to be equipped to obtain dyebath temperatures as close to 212°F as possible. Dark shades will build up more quickly, and staining of other fibers in the blend will be kept to a minimum. In addition, a maximum temperature will also insure uniformity from day to day, and remove the possible hazard of thermometer variations. Dye selection and retarding agents can be adjusted to insure the level dyeing of lighter shades.

TEMPERATURE CONTROL ——— To fully understand the Orlon dyeing picture, you should be aware that, although Orlon is considered a hard-to-dye fiber, it has rather high dye affinity. Once the temperatures of about 203°F has been reached, dye absorption can occur quite rapidly. Under practical dyeing conditions, as much as four to six degrees difference in temperature can be noted throughout a dyebath in this range. In addition to this, we also have the problem of uniform heat distribution throughout the folds of the goods being dyed. Surely the outside of a rope, or a bundle, will be heated more quickly than the inside. When this happens, if the outside is at 205°F and the inside at 195°F or even 200°F, you can see how the outer or hotter portion will accept dye more readily than the inner portion.

With respect to temperature control, one should keep in mind that, for Orlon acrylic fiber, the bath must be heated as uniformly over a 5° temperature range as it would be over a 100° range for, say, cotton, rayon, or wool. Instead of having 100 degrees over which the dye can be evenly absorbed, we have only five degrees.

DYEING TIME ——— When dyeing Orlon, or any other fiber for that matter, our objective is to apply color uniformly in a reasonable amount of time. Dark shades usually require a fairly lengthy period for the dye to build up in depth, while lighter shades tend to exhaust rather quickly. Whether dyeing a light or a dark shade, within any given time period during the initial phases of the dyeing cycle about the same amount of dye can be absorbed by the fiber. This quantity of dye may represent 90% of the total dye in the case of the light shade, but perhaps only five or 10% of the total dye in the heavier shade. This will be important to remember in the discussion of dye selection. In order to be fairly certain of obtaining a level dyeing, a good rule of thumb to follow is to set up the dyebath so that the dye will completely exhaust in not less than 45 to 60 minutes at maximum temperature.

DYE SELECTION ——— As we have already seen, quite a range of cationic dyes are available for dyeing Orlon, having a variety of dyeing rates. Since we have already seen that color buildup is a rate function, this can be directly tied to dye selection based on the dyeing rate of the individual dyes. The slower-dyeing colors are most suitable for light and medium shades, while the faster-dyeing types are best confined to heavier shades. Sometimes shade or fastness requirements necessitate mixing fast- and slow-dyeing colors, but this should be avoided whenever possible. There are certain exceptions to this which we will cover shortly.

Dye selection for various shade depths is best made from the groups illustrated in Table I. Opposite each dye is shown a figure representing the T/2 value for that dye. This figure,

assigned by DuPont to each of its cationic dyes, is the time in minutes required for one-half of the dye to exhaust on Orlon acrylic fiber, for a one percent dyeing, dyed with 6% DuPont Retarder LAN, at 206°F. More or less DuPont Retarder LAN, or more or less dye concentration and changes in temperature, will vary this figure.

The T/2 value is valuable for the selection of dyes used for starting dye formulations, or for selecting dyes for adding purposes. We will deal further with this later.

It is generally best to use dyes in combination that possess approximately similar dyeing rate. It is desirable to base dye selection on depth of shade also. Lighter shades require slow-dyeing dyes, while heavier shades use the faster-dyeing types. By doing this, retarding agent requirements are kept to a minimum, and dyeing times for the heavier shades are maintained within reasonable time cycles.

Dye selection for the light and heavy shades is fairly easy and can be based on the dye groups previously given. When it comes to medium-shade dye selection, some judgment based on knowledge of the individual dyes must be used.

Certain dyes are excellent for medium-shade work, such as Sevron Blue 5G, Blue NF, Red GL, Yellow 3RL, Brown YL, and CI Basic Blue 21. This is because of their moderate dyeing rate and good fastness properties.

Very often however, in the interests of economy, dyes listed for heavy shades can be used in medium shade depths.

CI Basic Green 4 is such a good value dye that it finds extensive use in such shades as charcoals and navies. In fact, wherever larger amounts of blue are required, CI Basic Green 4 is usually the base color. On the other hand, it would be unsatisfactory to use this dye in a shade requiring only a small amount of blue, even though it be a medium, or a medium-heavy shade.

This concept of dye selection also applies to other dyes. For example, a medium grey shade, requiring only a moderate amount of yellow, should utilize a dye such as Sevron Yellow 3RL rather than a dye such as Sevron Orange G.

The dyeing rate of an individual dye, or the T/2 value, must be considered in dye selection. It should be remembered that dyebath conditions must be set up to control the level dyeing of the fastest dyeing dye in the color combination, even though it represents only a small amount of the total dye present.

TABLE I

Typical basic dyes available for the dyeing of Orlon

Group I — For light shades

	T/2
Sevron Yellow GL	47
" Yellow 3RL	24
" Orange CL	32
" Brown YL	25
" Red GL	20
" Blue 2G (CI Basic Blue 22)	25
" Blue BGL	21
" Green B (CI Basic Green 3)	28

Group II — For medium shades

	T/2
Sevron Yellow R (CI Basic Yellow 11)	13
" Yellow 3RL	24
" Orange CL	32
" Brown YL	25
" Red GL	20
" Brilliant Red 4G (CI Basic Red 14)	14
" Blue B (Basic Blue 21)	17
" Blue NF	23
" Blue 5G	17
Victoria Green Small Crystals (CI Basic Green 4)	18

Group III — For heavy shades

	T/2
Sevron Yellow R (CI Basic Yellow 11)	13
" Orange G	10
" Brilliant Red 4G (CI Basic Red 14)	14
" Brilliant Red B	12
" Brilliant Red 3B	7
" Blue NF	21
Fuchsine Conc (CI Basic Violet 14)	23
Victoria Green Small Crystals (CI Basic Green 4)	18

A further example of dye selection might be a rust or yellowish brown shade. We would utilize either Sevron Blue NF, CI Basic Blue 21, or CI Basic Blue 22, rather than CI Basic Green 4 to supply blue in this instance.

We would recommend that a red shade requiring only a small amount of blue and yellow would be best made with Sevron Yellow 3RL and Sevron Blue NF or CI Basic Blue 22, rather than the faster-dyeing dyes listed for heavy shade work. In this manner the retarder requirements may be minimized and we would not risk unlevel pickup of the shading colors used.

PROCEDURE —— As mentioned earlier, the procedure for dyeing Orlon acrylic fiber should be based first of all on the maximum dyeing temperature attainable, then next on dye selection. The next step would be to set up the dyebath so that the shade builds up as uniformly as possible, and exhausts in not less than 45 to 60 minutes. This control of dyeing time can be adjusted readily by the use of an organic cationic product such as DuPont Retarder LAN in the dyebath. We should attempt to keep the retarder concentration as low as possible. Even though making the best dye selection, it is usually necessary to dye light shades with retarder in order to obtain the best level dyeing results. We suggest Retarder LAN be used in amounts of from 0.1% up to about 6%, based on the weight of Orlon acrylic fiber being dyed. In actual practice, it has been found often that, with proper dye selection, minimum amounts can be used. To determine the minimum amount of retarder, one should first dye with a maximum, then cut back on subsequent dyeing, until complete dye exhaustion occurs in about one to one and one-half hours.

In order to arrive at a percentage figure for Retarder LAN, we usually figure percent dye plus percent Retarder LAN should equal about 6 to 8%.

The percentage of older basic dyes, such as CI Basic Green 4 and CI Basic Violet 14, should be multiplied by four when making this calculation.

Another factor of dyebath make-up is pH. As you know, this can be rather important to several aspects of dyeing with cationic dyes. Dyes such as CI Basic Green 4 and CI Basic Violet 14 require acid for good solution. This, of course, indicates that basic dyes, in general, possess better solubility in an acid solution than they do in water. Too much acid can be harmful, and prevent dye exhaustion, while too little may contribute to poor solubility with resultant precipitation on the fiber. Poor crock- and wetfastness properties will result. It is extremely important that all the dye penetrate well into the fiber. The proper acidity will contribute to more complete dye exhaustion and penetration into the fiber, which in turn will promote less staining of other fibers that may be in the blend. It is generally suitable for the dyebath pH to be in the range of 4.0 to 6.0, but preferably in the range of 5.0 to 5.5.

Certain nonionic materials, such as Alkanol HCS, are valuable because they serve to improve the solubility of the basic dyes, and at the same time, assure little or no precipitation of the cationic dyes with any anionic materials which might be present. We know of instances where large amounts of this material have actually increased dyeing rate.

It is important, and often desirable, to scour Orlon acrylic fiber after dyeing. Here, in our opinion, the use of Alkanol HCS and acetic acid constitutes the most effective, nonstripping scour. Both products promote the solubility of any surface

(concluded on page 52)

Mid-West Section———

HISTORY OF NONWOVEN DEVELOPMENT AT 3M*

BURTON E FRANK
Gift Wrap and Fabric Div
Minnesota Mining & Mfg Co
St Paul, Minn

INTRODUCTION

A QUESTION many of you might want to ask is, "How did a firm with a background like that of Minnesota Mining and Manufacturing Company ever get into the nonwoven fabric business?"

Here was a company, which in the early 1940's was making notable progress in the fields of abrasives, adhesives, roofing granules, tape, etc. Actually, our original research work on nonwovens was done in the Tape Laboratory where a project was underway to find a backing with special properties for an electrical tape. From this work, a plied carded web, which we later sold as Mistlon brand ribbon, was developed. The first Mistlon was sold in the late fall and winter of 1944, on a trial basis, in a St Paul department store, at a time of severe ribbon shortage before the end of the war. The material was made by laminating several plies of garnett web of mixed acetate and viscose staple. Following the bonding operation, the carded web was dyed, stretched, waterproofed and dried.

Our Lacelon brand spun ribbon was introduced to the market in 1947, and Decorette brand, another spun ribbon, was introduced in its earliest form in 1948. These ribbons resulted from research work in spinning and cutting our own staple fiber for the manufacture of Mistlon.

To meet the competition from improved nonwoven ribbon constructions, which had been developed and placed on the market after the introduction of Mistlon, Sasheen brand ribbon was introduced late in 1949.

Part of our success in the ribbon field has been due to the accessories and the services we offer to our customers. Many types of racks and several bow machines have been introduced. Also, we have helped in the development of wrapping and banding equipment.

Now we are also marketing our own line of gift wrap paper, and have added many striped and printed patterns to our Sasheen and Decorette ribbon lines. It is no secret that, in our laboratory and pilot plant, we have several other ribbons under development or in pilot production. Also, of course, many other nonwoven applications are in various stages of research and development.

In the ribbon field we have several patents (USP 2,503,024; 2,620,853; 2,626,883; 2,738,298). Two pertain to Mistlon, another to Decorette, and a fourth covers Sasheen.

Originally the ribbon group was included in the Tape Laboratory. As we grew, we were made part of the Products Fabrication Laboratory; next, we became semi-independent, as the Carded Fabrication Laboratory. Later we were included in the Central Manufacturing Division, which supplies products, mainly resins, to be consumed internally in the company. We finally achieved sufficient size for division status and were converted to the Ribbon Division with a general manager. As the division diversified, it became necessary to find a more descriptive name for it, and we are now called the Gift Wrap and Fabric Division. In 1944, three people were employed in ribbon work. Now we have over 300.

The development of Sasheen Brand Ribbon will be my major topic, with special emphasis on our continuous dyeing method.

DISCUSSION

We consider Sasheen to be the top gift wrap ribbon available, the only exception being woven-edge satin, which now is seldom available at a price that makes it attractive for gift wrap. In our development work, we insisted that our ribbon should have certain properties, and these guided us in "building" the ribbon:

1) Nonsplitting. In other words, it must have sufficient crosswise strength to withstand normal handling when made into bows.
2) Nonfraying. This property is very important when notching and scissor styling bows.
3) Construction must collapse easily in the cross direction. It is important that the ribbon pull down into a small, compact knot.
4) High sheen. Of course we wanted the ribbon to be as attractive as possible.
5) Nonslip backing. This feature again is important in tying a small, tight knot that will not slip.
6) Ample strength.
7) Looks and feels like a fabric ribbon. We have always felt that a gift-wrap ribbon should have this characteristic.
8) Workability. This feature is contributed to by practically all the above-described properties. One of our selling points is the ease and speed of working with Sasheen. It ties into a tight, nonslip knot and pulls out readily in the form of bows with the loops staying put as they are pulled out.

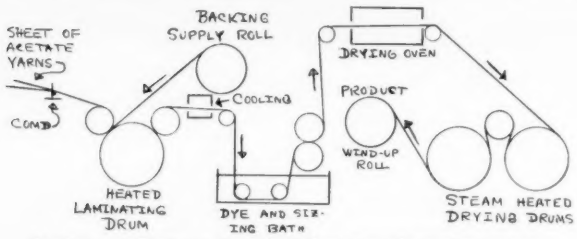
The ribbon is composed of a nonwoven backing, which is very similar to the old Mistlon Brand Ribbon, plus a high sheen surface of continuous filament cellulose acetate yarns.

Originally, the backing was made from a mixture of plasticized acetate staple and viscose staple, which were autogenously heat-bonded to form a continuous web of nonwoven material. Now we are using unplasticized acetate staple, blended with viscose, and adding the plasticizer ourselves. The mixed fibers are carded on a modified garnett machine, plasticized and dried. Subsequently, the yarns are heat bonded to the backing to complete the ribbon.

In our earliest production, we used 100-denier yarn, later we went to 150-denier, and now we are using 300-denier yarn of low twist. Following the bonding of the yarns to the backing, the unified ribbon is cooled and a dye-resin mixture is padded on. The dyes are dissolved in a solvent solution of 85 percent ethyl alcohol and 15 percent water in which a small percentage of an internally (structurally) plasticized resin has been dissolved. This resin, a special copolymer which we make within the company, is composed of 72 percent of vinyl acetate and 28 percent of 2-ethyl-butyl maleate. The excess solution is squeezed off by padding rolls; drying is accomplished in a flue and over heated cans. The final product, approximately 36 inches wide, is stored in the form of jumbo rolls for subsequent slitting to standard ribbon widths.

The development work on Sasheen occurred during 1948 and 1949. In the Laboratory we worked with yarns

* Presented before the Midwest Section on April 25, 1959, at the Schroeder Hotel, Milwaukee, Wis.



Outline of Sasheen brand ribbon-manufacturing process (not to scale)

which were rewound from commercial packages onto small sewing-machine-bobbin spools. We tried cellulose acetate yarns of 75, 100, 120, 150, and 300 denier. Our reasons for the final decision to use 300 denier was for strength (handling in our ribbon-making process), sheen, and, of course, price.

Our early samples of ribbon were made approximately ¾ of an inch wide and we graduated stepwise from this to three inches, six inches, 13 inches, 20 inches, and finally to the 36 plus inches of width we now make. I had little to do with the actual development of the ribbon, but as soon as samples were available they were given to me to check for a continuous dyeing method. It was evident very early in our development that we could not use the continuous dyeing method which had been so successful for Mistlon.

Our big problem was union dyeing of the acetate and viscose in a fast, continuous process. The question might well be raised by some of you as to why we use the viscose in our backing. There are several reasons: It increases backing strength and yet is never really bonded to the acetate. When the ribbon is stretched in processing (or "jerked" sharply when in actual use) the viscose tends to slip within the network of bonded acetate fibers, giving the ribbon a very desirable resilience. Also, the viscose provides bulk and adds to the opacity of the construction.

Our first Sasheen was dyed with tannic acid lakes of basic dyes. This gave brilliant colors and the required union dyeing, but was not entirely satisfactory because of poor lightfastness and a bronzing which occurred on the heavier shades. Our next step was to spirit soluble dyes. Again, we achieved union dyeing, but these colors were unsatisfactory because of water bleed and duller shades.

Our investigation of acetate dyes was spread over several years, and, as a matter of fact, is still going on. We have checked offerings from all the major suppliers, picking out the brightest, most soluble, and most lightfast dyes, testing always in our regular alcohol-water-resin mixture. At the present time, we dye Sasheen with these selected acetate dyes, which are actually crudes, with no extenders or dispersants added. Our first shades using the acetate dyes were introduced early in 1950, and were the lightest colors in our line because we could not obtain dyeing of the viscose with these dyes. We were, however, able to obtain sufficient staining of the viscose to give a satisfactory back-side appearance.

In order to color the medium and heavy shades with acetate dyes, we had to use precolored viscose in the backing. This, of course, created the need for additional inventories, in that a stock of colored staple, and backings with viscose in all these colors, had to be held on hand. Our first colored viscose was stock dyed, but more recently we have been able to obtain most of our shades in dope-dyed (spun-dyed) fiber. Many dye people have been surprised at the fine lightfastness we have been able to obtain with our continuous dyeing method. Pastel shades can take 24 hours of Fade-Ometer exposure, and darker shades are much better than this. For a product like ribbon, which is generally used once and then thrown away, these values of fastness are ample.

CONCLUSION

In conclusion, I would like to list our developments which are important in the nonwoven field:

1) A modified garnett carding machine, which is capable of quality web production with very high output poundage per hour.
2) The process by which we plasticize acetate staple in our backing material.
3) The continuous fast dyeing process for our completed Sasheen ribbon, which is developed to the point that we can run at 300 feet per minute.
4) The design and manufacture of machines for making bows and also the design of the bows themselves.

TRADEMARKS

Mistlon, Sasheen, Decorette, and Lacelon are trademarks of Minnesota Mining Mfg Co.

KNIT GOODS—

(*Concluded from page 50*)

dye from the Orlon or stain occurring on other fibers in the blend. Should a stronger cleanup be required, treatment with sodium hypochlorite, sodium hydrosulfite, or sodium sulfoxylate formaldehyde can be used. Since the bath should have an acid pH, it is perhaps best to avoid the hydrosulfite. Hypochlorite, of course, should not be used when wool is present.

CONCLUSION

Now, if all the dyeing and finishing operations are performed satisfactorily, and the garment manufacturer has done his job well, the results are seen by the public as some of the fashions we have here.

I feel sure you will agree that, in spite of the dyeing and finishing problems, the final result as seen in public has been well worth the effort.

In closing let me say that you men, as dyers and finishers, can contribute to the success of your company, and assist in promoting better business, by making it your job to point out to your management how modern fibers and coloration techniques can be used. Too often in the past the dyer has been given a coloration job that has not been practical, or perhaps has been designed by someone without a good background in practical dyeing. Often there is an easy way and a hard way to obtain a desired effect.

It should be up to the dyer to point the way, and be certain that his management and styling people are aware of color possibilities, and how various fibers, such as Orlon acrylic fiber, can be used to their advantage.

TRADEMARKS

The following registered trademarks of E I duPont de Nemours & Co, Inc, have been used in the paper: Orlon, Dacron, Alkanol, Latyl, Celanthrene, and Sevron.

1959 AATCC NATIONAL CONVENTION

October 8, 9, 10 • Hotels Sheraton-Park & Shoreham, Washington, D C

WASHINGTON CONVENTION TO FEATURE EXHIBITS

INVITATIONS to exhibit at the 1959 AATCC National Convention have been issued and the response indicates that there will be a sell-out of exhibition space before Convention time.

The 1959 Convention exhibits will open on Wednesday, October 7th at 4 PM for a preview. Exhibitors and others who can register on Wednesday before the Convention officially opens on October 8th are encouraged to do so to avoid the slight delay indigenous to the registration problems on the morning of the opening day.

Any individual or firm wishing to exhibit products or services to an anticipated audience of approximately 2,000 and not having received application forms for exhibits, may contact Exhibits Chairman George P Fulton, general manager, National Institute of Drycleaning, Silver Spring, Md by letter or phone.

A copy of the exhibit floor plan of the Sheraton-Park Hotel is shown. Assignment of space will be made in the order that applications are received. Exhibit space will be rented on a basis of $3.00 per sq ft for the duration of the Convention. Confirmation of assignments will be sent to exhibitors promptly.

GEORGE P FULTON
Chairman
Exhibits Committee
1959 AATCC Convention

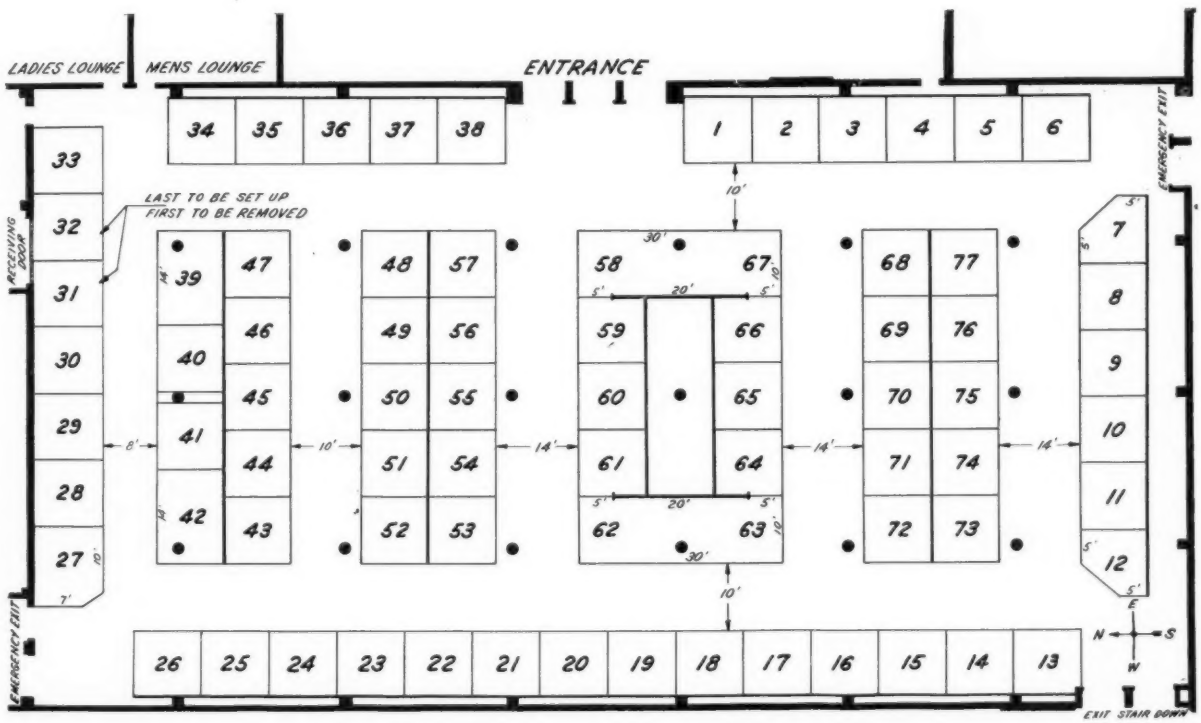


Exhibit Floor Plan, Sheraton-Park Hotel, Washington, DC

AATCC Calendar

COUNCIL, COUNCIL COMMITTEES, RESEARCH COMMITTEES

Sept 10-11 (Hotel McAlpin, New York, NY); Sept 10—Council Committees and Research Committees; Sept 11 (AM)—ECR, TCR; Sept 11 (PM)—Council

NATIONAL CONVENTIONS

Oct 7-10, 1959 (Sheraton Park and Shoreham Hotels, Washington, DC); Oct 6-8, 1960 (Sheraton Hotel, Philadelphia, Pa); September 28-30, 1961 (Buffalo, NY); 1962 (Southern Region)

DELAWARE VALLEY SECTION

Sept 18 (Reading, Pa); Oct 23 (Kugler's Restaurant, Philadelphia, Pa.

MID-WEST SECTION

Oct 24 (Bismarck Hotel, Chicago, Ill)

NIAGARA FRONTIER SECTION

Sept 25 (Niagara Falls, Ont, Canada); Dec 11 (Annual business meeting, Buffalo, NY)

NORTHERN NEW ENGLAND SECTION

Sept 25 (Outing—Wachusett Country Club, West Boylston, Mass); Oct 16 (Lexington Inn, Lexington, Mass); Dec 4 (Joint symposium with ASME Textile Engineering Div, Smith House, Cambridge, Mass); Jan 15 (Woodlawn Golf Club, Newton, Mass)

PIEDMONT SECTION

Sept 25-26 (Barringer Hotel, Charlotte, NC); Jan 22-23 (Poinsett Hotel, Greenville, SC); April 2-3 (Hotel Robert E Lee, Winston-Salem, NC); June 3-4 (Outing—Ocean Forest Hotel, Myrtle Beach, SC); Sept 23-24, 1960 (Hotel Charlotte, Charlotte, NC)

RHODE ISLAND SECTION

Sept 18 (Management Night); Oct 23 (Prov Eng Soc, Providence, RI); Dec 4 (Annual Meeting—Johnson's Hummocks Grille, Providence, RI)

SOUTH CENTRAL SECTION

Sept 19 (Hotel Patten, Chattanooga, Tenn)

SOUTHEASTERN SECTION

Sept 12 (Ida Cason Callaway Gardens, Pine Mtn, Ga); Dec 5 (Atlanta Athletic Club, Atlanta, Ga)

WESTERN NEW ENGLAND SECTION

Sept 25 (Blake's Restaurant, Springfield, Mass); Oct 23 (Annual Meeting—Rapp's Restaurant, Shelton, Conn); Dec 4 (Hartford, Conn)

Activities of the Local Sections

Northern New England

THE annual joint meeting of the Northern New England Section and the Lowell Technological Institute Student Chapter, held May 15th at the Institute, featured afternoon and evening programs, both of which were handled by LTI Student Chapter members.

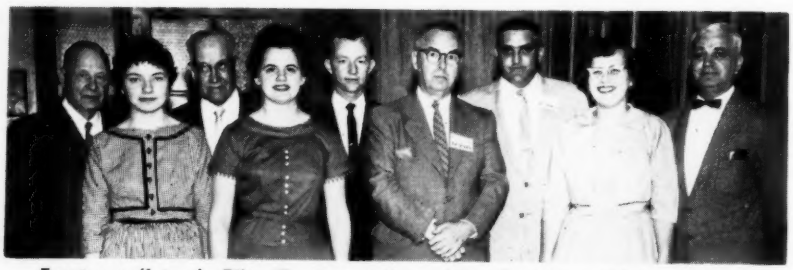
The afternoon program, under program chairman Gertrude Long, was held in Southwick Hall. The following experimental pilot-plant operations were shown: Emulsion Dyeing of Dacron 54, illustrating the process which was to be discussed during the evening program, by Georgia Dadoly and James Casey; Continuous Naphthol Dyeing on the Williams Unit, by John J Swistak; Application of a Reactive Dye on Wool, by R Carl Freeman; and Vat Dyeing on the Jig, by L Donald La Torre.

Toby Koffman was in charge of the evening program, which featured three papers.

Georgia Dadoly and James Casey, LTI seniors, presented the results of a study of the dyeing of Dacron by dyes dissolved in organic solvents which are emulsified in water.

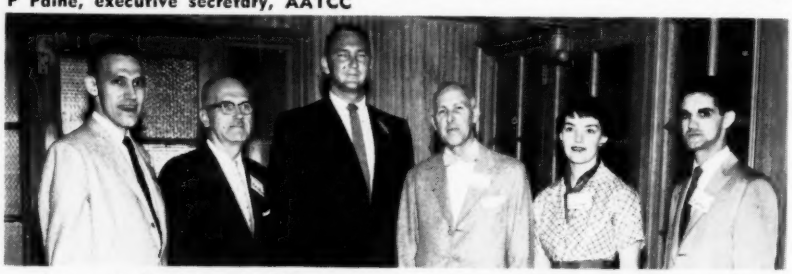
Prof John H Skinkle of LTI, in his paper, "The Dyeing Properties of Dye Isomers," discussed the effect on rate and exhaustion of the position of organic radicals in the dyestuff molecule.

"A Preliminary Study of Dyeing Systems Subjected to Ultrasonic Vibration," a paper which is part of a thesis to the MS degree, was presented by Robert E Morrison, LTI instructor.



Front row (l to r): Ellen Trevors, student; Aline Fournier, student; Prof John H Skinkle, LTI, speaker; Georgia Dadoly, student speaker; Gerald F Quigley, Councilor, NNE Section. Rear row (l to r): Elmer E Fickett; George O Linberg, past president, AATCC; James Casey, student speaker; Robert E Morrison, LTI, speaker

L to r: Stanley Sledziewski, student; Francis Davis, student; Joseph S Panto, secretary, NNE Section; Daniel Frishman, chairman, NNE Section Intersectional Contest Committee; Toby Koffman, student chairman of evening session; George P Paine, executive secretary, AATCC



L to r: R Carl Freeman, LTI student recipient of AATCC Book Prize; W George Parks, vice president, AATCC; Edward J McNamara Jr, vice chairman, NNE Section; Robert D Robinson, chairman, NNE Section; Gertrude Long, student chairman of afternoon session; John J Santos, chairman, LTI Student Chapter

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JULY 1, 1959

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Membership Applications

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Bernard Rubinowitz — President, Peerless Color Co Inc, Plainfield, NJ. Sponsors: H A Stauderman, R E Miller.

Mitchell J Rudolf—Asst editorial dir, Use-tested program, McCall Corp, New York, NY. Sponsors: A J Kellner, C A Baker.

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George H Wahl Jr — Research chemist, textile bleaching, Columbia-Southern Chem Corp, Barberton, Ohio. Sponsors: R R Currier, C J Stroemple.

Associate

James R Arthur—Tech dir, Port Huron Sulphite & Paper Co, Port Huron, Mich.

Student

William E Helmick—Lab tech, textile bleaching research, Columbia-Southern Chem Corp, Barberton, Ohio. Sponsor: R C Gagnon.

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John T Williams—Overseer, dyeing & finishing, Riegel Textile Corp, Trion, Ga. Sponsors: E A Freeman Jr, W J Welborn.

UNASSIGNED
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Giuseppe Briganti — Asst mgr, Bleaching Section Cotonificio Cantoni SpA, Stabilimento oli Castellanza, Castellanza Varese, Italy. Sponsors: M Ferrari, O M Lea.

Jim Woo Rhee—Teaching asst, Dept of Textiles, College of Engineering, Seoul National Univ, Seoul, Korea. Sponsors: J J McDonald, G Kidder.

Transfer to Associate

Ibrahim Yuceyar—Tech dir, Tarim Sokak # 20, Bornova-Izmir, Turkey.

Future Papers

THE following list is comprised of papers submitted to date for publication in future issues of the *Proceedings*. Authors and Technical Program Chairmen are requested to examine this list and call our attention to any omissions.

"Practical Experience with the Pad-Roll Dyeing Machine"—Robert M Lesh and Frank Percarpio, Northern Dyeing Corp; John S Thackrah, E I duPont de Nemours & Co, Inc

"Instrumentation—An Integral Part of Dyeing and Finishing"—Walter H Ridley, Foxboro Co

"AATCC Looks Ahead"—Charles A Sylvester, chairman, Technical Committee on Research

Committee reports presented at joint AATCC - CATCC Technical Session.

Additions and Amendments to the *Colour Index*—No. 4

CORRECTION

RECENT publicity releases concerning the 1959 AATCC Convention have listed George H Lourigan, chairman of the Transportation Committee, as affiliated with Harris Research Laboratories, Inc. This is incorrect.

Mr Lourigan is an employee of Union Carbide Chemicals Co. However, his mailing address at the present time is Harris Research Laboratories, Inc, 6220 Kansas Ave, NE, Washington 11, DC.

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• PATENT DIGEST •

RESTORING WHITENESS TO YELLOWED NYLON ——— Hypochlorite treatment G,1

USPat 2,830,868 (Clorox Co——Barton——April 15, 1958)

The preamble to this patent states that age-yellowing of nylon fabrics cannot be prevented by the application of regular oxidizing or reducing bleaching agents. Whitening effects produced with fluorescent dyes (Blancophors or the like) reportedly are unstable so that the yellow tint reappears after a short time.

It is claimed that stable whitening of nylon fabrics may be attained by using controlled amounts of sodium hypochlorite plus an organic acid, such as citric or acetic acid. Strict control under conditions mentioned below is imperative.

To one gallon of water at approx 125° F, one ounce of a 5.25% sodium hypochlorite solution and ⅛ ounce of household vinegar (content approx 5% acetic acid) are added. After this solution is mixed, the yellow fabric is immediately immersed and kept therein for 15-40 minutes, depending on the intensity of the shade, then removed and rinsed. The effect reportedly persists for three to four months, a period similar to that for new, nontreated nylon to turn yellow. The pH is optimum between 7.7-8.7.

Among the references cited by the Patent Office:

USPat 2,105,839 (Tubize-Chatillon/1938): bleaching artificial silk with hypochlorite solutions neutralized with acetic acid, boric acid or the like.

USPat 2,727,804 (Onderzoek Inst Research/1955): bleaching polyamide yarn with hypochlorite solutions followed by a treatment with reducing agents at temperatures above 80° C.

CREASEPROOFING OF COTTON OR RAYON ——— Dialdehydes plus catalysts applied and cured G,2,04

USPat 2,826,514 (Shell Development Co——Schroeder——March 11, 1958)

The object of the current invention is to provide a new process for rendering cotton or rayon crease resistant without impairing the tensile strength while at the same time avoiding any of the deleterious effects frequently observed in finishes based on amino resin condensates, such as yellowing, chlorine retention, etc.

It has been found that preparations with aliphatic dialdehydes (alkanedials) of chain length 5-8 C atoms, containing certain metal salts as curing agents and, optionally, polyalcohols, produce highly crease-resistant effects while avoiding the above-mentioned disadvantages.

PAUL WENGRAF

The use of glutaraldehyde . . . HOC—$(CH_2)_3$—COH . . . , which is protected by the claims, is preferable, but adipaldehyde or suberaldehyde might also be used. The dialdehydes are made generally water soluble or at least dispersible by applying, eg, monooleate of polyethoxylated sorbitan (Tween 80) as emulsifier. Agents containing nitrogen or strong acidic groups must be avoided.

Catalysts called for are salts of non-alkaline metals of atomic weight 24-207 with anions containing at least two dissimilar elements; one of them being B, Si, S or P and the other one, O, F or Cl. Examples are zinc-, cadmium-, or copper borate and magnesium perchlorate, which are cited in most of the examples.

Polyalcohols such as glycerol, trimethylolpropane or pentaerythritol were found to give unexpected resistance to discoloration.

Example: An aqueous solution of glutaraldehyde, magnesium perchlorate and glycerol (20% on weight of glutaraldehyde) were padded on rayon cloth, which was subsequently dried at 60° C for five minutes and cured at 160° C for another five minutes, then washed in a soda ash-soap solution at 70° C for 12 minutes. The wrinkle recovery of the cloth proved to be superior to that obtained with glyoxal or with hydroxy adipic aldehyde. The treated cloth reportedly showed good white appearance without any tendency towards discoloration.

Among the references cited by the Patent Office:

USPat 2,436,076 (Cluett Peabody/1948) covers a process for the stabilizing of fibers containing predominantly regenerated cellulose by an acid-catalyzed glyoxal treatment. [Cf *Am Dyestuff Reptr 37*, 475 (1948)].

USPat 2,774,691 (Shell Development-Schroeder/1956): shrink- or crease-proofing textiles by applying mixtures of epoxy resins and polyaldehydes and curing under acid conditions. A great number of polyaldehydes is enumerated in col 7 of this specification, but products are restricted in the claims to dialdehydes C_2-C_4.

Fr Pat 1,058,002 (Allgem Kunstzijde/1954: shrinkproofing rayon material by applving a dialdehyde of five or more C atoms chain length, preferably OH-adipic aldehyde, and catalyzing with an organic acid (oxalic).

PREVENTING YELLOWING OF NYLON ——— Treatment with urea and other N-organic compounds G,1

USPats 2,823,093-4 (Rohm & Haas——Steiger ——Feb 11, 1958)

It is known that nylon yellows on aging and also as a result of heating operations, such as ironing, curing or baking.

According to USPat 2,823,093, discoloration or yellowing of nylon upon heating can be reduced or completely eliminated by preparing the goods with aqueous solutions of urea, dicyandiamide, biuret and ammonium cyanate, and then heating the thus-treated materials to a minimum temperature of 240° F, up to a maximum of 450° F. This effect is particularly significant in combination with any one of the known aminoplast finishes, eg, with urea-formaldehyde condensates. Nylon goods first prepared according to the patented method and subsequently treated with one of the customary creaseproofing or stiffening resin finishes reportedly do not show any discoloration upon heating in contrast to normal aminoplast finishes.

Example: A scoured nylon taffeta was padded after drying in a 30% urea solution, air dried and cured at 300° F for 10 minutes, rinsed to remove nonreacted urea, and air dried again. This specimen showed only slight discoloration upon being heated to 300° F for five hours while a control sample reportedly exhibited strong discoloration.

According to USPat 2,823,094, this process may be further modified by impregnating and heating in one step. The goods have to be treated in an aqueous solution of one of the above N-compounds (minimum concentration 15%) for at least one-half hour at 90-150° C.

Among the references cited by the Patent Office:

USPat 2,458,397 (Courtaulds/1949): increasing the affinity of nylon for direct dyes by incorporating a water-insoluble condensate of formaldehyde with cyanamide, dicyandiamide and other bases of this group. [Cf *Am Dyestuff Reptr 38*, 363 (1949)].

Brit Pat 547,844 (Courtaulds/1942): direct dyes with otherwise poor affinity for nylon reportedly dye nylon in full shades when various phenols, anilides, sulfonamides, etc, are added to the bath.

CONTINUOUS VAT-DYEING PROCESS——Increased alkali content of dyebath C,4,02

USPat 2,827,357 (Standfast Dyers & Printers Ltd ——Hannay, Kilby——March 18, 1958)

This patent, which covers a continuous vat-dyeing process for all kinds of vegetable fibers, is characterized by the use of a dye liquid of unusually high alkali concentration in the range of 120 g up to 400 g (preferably 200 g) caustic alkali pro lit. The alkali may be NaOH, KOH, sodium zincate or any other alkaline substance that will act as a swelling agent on cellulose. A 50% reduction in dyestuff costs with some dyes has been claimed. Thus with this method the total consumption of dye reportedly is much less for a given material and shade than is the case when the goods are dyed by the customary continuous vat-dyeing process.

The current method may be preferred in conjunction with the Standfast Molten Metal Process described in Brit Pats 620,584; 661,086; 681,983; 665,454 and 663,066. [Cf *Am Dyestuff Reptr 41,* 442 (1952) and *41,* 306, (1952)].

Example: Dry unscoured cotton yarn in tape form was heated to approx 80°C by passing over steam-heated cylinders, then introduced in a small volume of an aqueous dye liquor (75° C) floating on the surface of a molten metal bath, and passed at the outlet through a 10% hot Glauber's salt solution, oxidized, soaped and rinsed as usual. The dyebath contained 100 g CI Vat Red 35 (1-2-anthraquinone naphtacridone), 200 g caustic soda per liter, sodium hydrosulfite, glucose syrup and appropriate wetting and dispersing agents. The red shade proved to be 50% darker than that of a control sample in which normal amounts of alkalis (15 g/l) had been used.

Among the references cited by the Patent Office:

Ger Pat 99,337 (Farbenfabr Bayer /Sept 13, 1898): some sulfur dyes are added to a high concentrated caustic soda solution, thus dyeing and mercerizing at the same time.

Reference may also be made to Brit Pat 473,353 (Ciba) covering the use of unusually strong alkalis in printing with difficult-to-print vat dyes.

SHRINKPROOFING OF WOOL ——— Insolubilized copolymers of 4-vinylpyridine applied A,2,04

USPat 2,827,359 (Rohm & Haas——Kine, Matlin ——March 18, 1958)

This patent is concerned with the preparation of stable aqueous dispersions of copolymers of 4-vinylpyridine with another polymerizable monomer, such as acrylic or methacrylic acid esters, vinyl esters of fatty acids, alkylvinyl ethers, and so on. Wool (or other proteinaceous fibers) are impregnated with these dispersed copolymers and heated to at least 212° F, where a reaction between the protein and the copolymer reportedly takes place, so that the firmly bound resinous copolymer can no longer be removed from the fiber by washing or drycleaning.

4-Vinylpyridine has been found to be unique in forming copolymers of the above type, having a superior shrinkproofing effect in comparison with other vinyl or alkylvinyl pyridines. The copolymers must not be water-soluble. The upper limit of the content of 4-vinylpyridine depends on the degree of solubility of the other comonomer. Prior to copolymerization, the monomeric emulsions of both components are prepared with emulsifying agents of the anionic or nonionic group. A particularly valuable dispersion can be obtained by emulsifying a mixture of the monomers and polymerizing the mixture while it is in emulsified form. Preferred catalytic systems are those of the Redox type, ie, combinations of oxidizing agents (persulfate) with reducing agents.

Example: Ninety pbw n-butylacrylate and 10 pbw 4-vinylpyridine were dispersed in 300 p water, using polyethoxylated octylphenol as emulsifier. 0.3% Ammonium persulfate, 1% triethanolamine and 0.06% sodium hydrosulfite (on weight of the monomers) were used to catalyze the reaction. The solution was diluted to a copolymer resin content of 13.5%, then padded on wool flannel, which was dried at 240°F and cured for 10 minutes at 300°F. Shrinkage of the fabric, after a five-hour soap wash in a Cascade wheel washer was found to be zero.

Among the references cited by the Patent Office:

USPat 2,406,412 (Imp Chem Ind/-1946): exposing wool fibers to vapors of volatile monomeric polymerizable monovinylidene compounds, such as methyl methacrylate, to increase the shrink resistance.

USPat 2,499,653 (Am Cyanamid/-1950): shrinkproofing of proteinaceous textiles by a treatment with a reactive product of copolymerization of maleic anhydride with a major amount of lower alkyl-acrylic esters. [Cf *Am Dyestuff Reptr 39,* 338 (1950)].

Brit Pat 611,828 (Wolsey Ltd/1949): shrinkproofing of woolen material by impregnating first with a cationic emulsifying agent (Fixanol or the like) and, in a second step, with an emulsion of a resinous vinyl polymer. (Vinylpyridines are not mentioned).

FLAMEPROOFING OF TEXTILES ——— Combination of amidophosphates and methylolmelamines G,2,03

USPat 2,828,228 (Am Cyanamid Co——Glade, Hechenbleikner——March 25, 1958)

The preamble to this patent stresses the widespread demand for effective fire-retardants that are durable to severe alkaline washes and applicable without discomfort, and require no special safety precautions.

According to this patent, a fire-retardant finish for cellulosic textiles which will fulfill the above requirements is comprised of

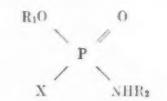
a) a methylolmelamine or an alkylether thereof,

b) an alkylamidophosphate, and

c) an acid curing agent whenever the component "b" should not contain certain amounts of ammonium chloride and ammonium phosphate (optional).

Methylolmelamines or low-alkylated methylolmelamines suitable for this method are enumerated in col 1, line 12 to col 2, line 41. Dimethylated trimethylomelamine proved to be outstanding in the present case. Included also are the known melamine condensates in acid colloidal form as described in USPat 2,345,543. (Cyanamid-Wohnsiedler).

Alkylamidophosphates have the schematic formula:



wherein R_1 is lower alkyl, alkoxyalkyl or halogenated alkyl; R_2 is H or lower alkyl; and X is the oxyalkyl or alkylimido group. A series of these compounds is reported in col 2, line 42 to col 3, line 3. Examples include dimethyl-, diethyl- and dibutylamidophosphates. Purification of these products to remove ammonium chlorides and ammonium phosphates (see col 3, lines 14-37) is required only in cases where especially long shelf life is desired.

Generally, the three above-mentioned components are added separately to the padding bath without previous purification. The finish is cured by heating to 200-500°F (preferably 250-375°F) for 10 seconds to 30 minutes. The impregnating baths should be slightly acid. A deposit of about seven to 20% of the alkylamidophosphates and five percent of the methylolmelamines on the dry weight of the fabrics is preferred.

Various curing catalysts, such as acids, ammonium salts, etc, are in-

dicated in col 4, lines 49-75.

The chemistry of this reaction is not quite understood because neither component "a", which in turn reacts provide any fire protection. It is believed that component "b" links with component "a", which in turn reacts with a reactive hydroxy group of cellulose.

Example: Cotton poplin, which would burn completely when subjected to the AATCC vertical flame test, was padded with aqueous solutions of 15% dibutylamidophosphate and 15% dimethylated trimethylolmelamine with an 85% wet pick-up, dried and cured for six minutes at 290° F. After it was washed in five subsequent cycles with soap and soda ash, excellent flameproof, crease and shrink resistance, afterglow and tensile strength properties were noted. (See Tables I and II in col 6, lines 32-53 and col 7, lines 3-19 respectively).

Among the references cited by the Patent Office.

USPat 2,574,516 (Glenn Martin/1951) describes the preparation of aliphatic amino phosphine oxides, eg, diallylamino phosphine oxide, and their use as flame retardants.

USPat 2,596,937 (Monsanto Chem Co/1952): polyphosphorylamides, prepared according to USPat 2,596,935 (Monsanto), ie, by reacting anhydrous ammonia with phosphorus oxychloride in an inert medium, are used in combination with resinous condensates of formaldehyde with urea, dicyandiamide or melamine as fire retardants.

FLAMEPROOFING OF CELLULOSIC FIBERS ——— Condensates of amidophosphoric esters and trimethylolmelamines with allylphosphate adducts G,2,03

USPat 2,832,745 (Shea Chem Corp——Hechenbleikner——April 29, 1958)

The preamble to the current patent refers to flameproofing compositions based on adducts of bromoform and triallylphosphates, which reportedly give finishes of insufficient fastness to laundering. These adducts can also be combined with THPC flameproofing agent (tetrakis hydroxymethyl phosphonium chloride). Compositions of this type were found to be expensive, to develop objectionable odors, and to have a relatively low content of phosphorus.

It is claimed in the present patent that the problem of providing a more economical and stable flame-retardant finish may be met by combining

a) the adducts of bromoform and triallylphosphate with

b) an aminophosphoric acid dialkylester, preferably diethylphosphoramidate of the formula

$$(C_2H_5O)_2\,P(=O)-NH_2,$$ and

c) trimethylolmelamine.

Surprisingly, it may be noted that "b" and "c" may cause severe tendering of cellulosic textiles, imparting a stiff boardy hand to the goods, when component "a" is omitted. However, all three combine to give improved flexibility and superior flame resistance, probably by formation of a thermosetting resin within the textile.

Example: Equal parts of "b" and "c" were dissolved in water and "a", emulsified in polyvinylalcohol (medium viscosity), and sodium bicarbonate and water were stirred in until a homogenous emulsion resulted. Upon the addition of potassium persulfate, component "a" polymerized and the entire emulsion was adjusted to pH 5-6. Cotton cloth impregnated in this solution was dried at 80°C and cured for three minutes at 160° C. The sample was found to be flame resistant, even after 20 launderings.

Among the references cited by the Patent Office:

USPat 2,574,516 (Glenn Martin/1952): unsaturated aliphatic phosphonamide derivatives, such as diallylphosphonamide, may be used as flameproofing, fungicidal and insecticidal agent.

USPat 2,582,961 (Am Cyanamid/1952): rendering textiles flame resistant by applying mixtures of heat-curable methylolmelamine condensates, methylol dicyandiamide, and an oxygen-containing phosphorus acid (o-phosphoric acid), and curing.

PIGMENT PRINTS ——— Fixation with condensates of polyepoxy compounds D,2,07

Brit Pat 787,032 (Imp Chem Ind——Cooper et al ——Nov 27, 1957)

Pigmented prints, impregnations or coatings are fixed on fibrous materials by aqueous solutions of condensates of an epoxide having an "average functionality" greater than one, a synthetic polymeric material containing reactive OH or COOH groups, and a basic catalyst.

The "average functionality" is defined as the average number of epoxy groups per mol of epoxide. Simple and polymeric types that contain more than one epoxy group may be applied. An example of a simple epoxide is 1:2-3:4 diepoxybutane. These polyepoxides may also be blended with monoepoxides, eg, 2:3 epoxypropylether. Examples of polymer epoxides are those obtained by polymerizing unsaturated epoxides, eg, 3-4-epoxy-1-butene, and similar compounds. (Cf p1, line 25 to p2, line 61).

Examples of the synthetic polymeric materials mentioned above are insoluble polyesters, eg, adipic esters of polyalcohols; water-soluble substances, such as polyvinylalcohols; or aqueous dispersions from vinyl copolymers containing minor amounts of carboxylic acids, eg, copolymers derived from methacrylic acid, the latter being preferred.

A great variety of basic catalysts (enumerated on p2, line 24 to p3, line 38) may be applied. Tritertiary amines, for instance, 2:4:6-tri(dimethylaminomethyl) phenol, were found to be particularly effective. Alkalimetal hydroxides and quaternary ammonium compounds are also useful.

An insoluble polymer is produced by heating aqueous solutions or dispersions of the above three components after they are applied to textile material. The time of heating should be as short as possible, eg, a few minutes, and temperatures must not exceed 160° C.

Example: 2:2 di[4-(2:3) epoxy propoxy phenyl] propane was stirred with a 24% aqueous solution of a copolymer of methacrylic acid and ethoxy-ethyl methacrylate, and neutralized to 80% of the free carboxylic groups with NaOH. Tris(dimethylaminomethyl) phenol was added to the smooth emulsion and an aqueous suspension of copper phthalocyanine was stirred in. The paste so obtained was printed on cotton, dried and heated for one hour to 100° C. A blue pattern reportedly fast to soaping resulted.

Reference may be made to USPat 2,762,718 (Farbenfabr Bayer/1956), which describes pigment fixation with resins containing epoxy condensates. [Cf *Am Dyestuff Reptr 46, 375* (1957)].

ANTISTATIC TREATMENT ——— Unsaturated esters polymerized in the presence of boron compounds G,1

USPat 2,841,567 (Union Carbide Corp——Blanton, Field Jr——July 1, 1958)

The preamble to this patent refers to a static-preventing method based on the use of polymerizable esters of polyethylene glycols plus appropriate free-radical-generating catalysts, followed by a treatment for removing the water from the solutions. While these compositions were found to be very effective at the start, increased viscosity and even gelling of the substance occurred in the containers upon storage.

In contrast, this latest patented method reportedly provides for compositions which are stable in storage.

They contain the active antistatic component in concentrated form and are substantially free from catalysts at the moment of their use so that no discoloration of the fabrics is said to occur.

These compositions consist of

a) polymerizable monomers of unsaturated esters of polyethylene glycols,

b) an inorganic boron compound, and

c) a polymerization catalyst.

The preferred monomer has the constitution . . . CH_2 : $CH.COO(CH_2-CH_2O)_n$ R . . . , wherein "R" in hydrogen or the acrylic chain prepared by the reaction of polyethylene glycol and acrylic acid in the molar ratio 1 : 1.5 in benzene solution in the presence of an acid catalyst.

The inorganic boron compound may be borax, boric acid and so on. It must be added to the aqueous solution (a) before polymerization and concentration of the solution is started. The boron compound appears to assist polymerization and to prevent gelling.

The catalyst may be peracetic acid, hydrogen peroxide, or mixtures thereof.

These agents are claimed to be particularly useful on hydrophobic textiles formed from acrylic or vinylic polymers (col 1, lines 25-33). The concentrated solutions are diluted with water to a solid content of 0.25-10% and applied to textiles by standard procedures. The textiles so treated are dried at 70-120° C. Under these conditions, the monomer is converted to an insoluble polymer, which firmly adheres to the fiber's surface. Permanent, wash-resistant, antistatic effects are said to be obtained with the application of 4% or more owf.

Example: Mixed acrylate esters of polyethylene glycols (average mol weight 600) were dissolved in water at the ratio of 400 : 1576 and 2-32% borax (of the esters' weight) was added. Thereupon a mixture of aqueous peracetic acid and hydrogen peroxide (5.3% of the esters' weight) was introduced. The solution, at a pH of 4.8, was concentrated by heating to the boil until the solid content was 43.44% (pH 5.6) and later adjusted to pH 7 with NaOH. A table reports favorable results regarding the antistatic effect immediately upon application and after ten and fifteen washes respectively.

Among the references cited by the Patent Office:

USPat 2,375,140 (B F Goodrich Co/1945): among the salts used to prevent gelling in emulsion polymerization of butadiene 1-3-hydrocarbons are water-soluble borates (see p2, right col, line 57).

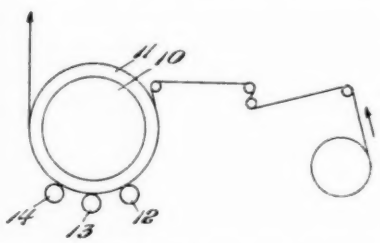
USPat 2,628,178 (Gen Electric/1953) describes the production of specific monomers, eg, tetraethylene glycol dimethacrylate, which can be oxygenated readily in an oxygen current to produce a different polymerizable material.

TEXTILE PRINTING METHOD using extremely shallow photogravure engravings D,6

Brit Pat 788,635 (Apponaug Co——Jan 2, 1958)

According to the introduction to the present specification, the photoengraving technique used in printing of paper has not hitherto been applied successfully to printing of textiles. Paper prints obtained from shallow engravings show the very fine details of a design, while printing effects of the same quality can not be achieved on regular textile printing equipment. The principal reason is that paper has an inherent flatness and smoothness, which allows the finest lines of a pattern to be shown, in contrast to the usually coarse and uneven surfaces of the cloth. Further, printing equipment for paper provides for a smooth, rubber-coated backing metal cylinder in contrast to the more or less uneven surface of a backing roller covered with coarse fiber lapping and the customary textured fiber-rubber blanket used in textile-printing techniques.

The current invention aims to incorporate the advantages of the paper-printing technique to a textile printing process while using standard textile-printing equipment. To print on a surface simulating the smooth, flat nature of paper, it is necessary to choose a cloth of proper smoothness, or preferably, by precalendering the fabric, to impart temporarily a flat surface. To simulate the equally smooth backing roller, the usual blanket and lapping-covered cylinder is replaced by an iron roller (10 in illustration) provided with a heavy rubber covering (11), as employed in paper-printing technique. However, in contrast to paper-printing machines, only the engraved rollers, (12, 13, 14) are used for driving the main roller (10) by contact, like in customary textile printing procedure.



Printing with an engraved roller of normal depth (0.03-0.05 inch) would necessarily cause smearing on the smooth cloth supported by the flat rubber surface described above. Thus, an essential feature of the present invention is the use of extremely shallow, photographically produced engravings of depth ranging from one micron to maximum 0.001 inch. Engravings of this type are often referred to as rotogravures or photogravures. Continuous tone graduations like those in photography reportedly are produced this way.

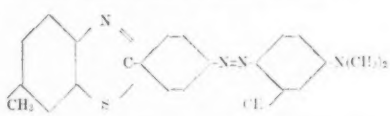
Printing pastes adaptable to the present method are characterized by a far lower viscosity—from 200 to 3000 centipoises—than those used in conventional printing pastes, which generally have a viscosity of 6000 to 8000 cp. Otherwise, all kind of vats, pigments, etc, may be applied. Formulations for regular aqueous vat-printing pastes, resin-fixed pigments, sulfur, disperse and acid colors are presented with all necessary details.

DYEING OF POLYACRYLONITRILE FIBERS with unsulfonated azodyes containing a cycloammonium group C,4,07

Brit Pat 789,263 (J R Geigy A G——Jan 15, 1958)

According to the preamble to this specification, attempts to dye polyacrylic textiles with sulfonated azo dyes in the presence of cuprous ions have had some success, but levelness of the dyeings has been found to be insufficient.

It has been observed that azodyes that contain cycloammonium groups instead of acid solubilizers as water-solubilizing radicals provide good levelness and pure, fast shades. A great number of dyestuffs characterized by a component containing an ammonium N-atom of the cycloammonium group are within the scope of this invention. A typical example is the (insoluble) mono azodye



which may be solubilized by quaternization with dimethylsulfate and applied from a dyebath containing sodium acetate, acetic acid and a non-ionic assistant. A full, wine-red shade of excellent fastness to water and light reportedly results. (Example #1, page 3). The cycloammonium group is formed here by quaternizing the methyl benzthiazole component (left hand part of the above formula).

Shades obtained vary according to the nature of the coupling component and the quaternizing agent. (See tables on pages 3-11 of this specification).

Staley Acquires UBS Chemical

The A E Staley Mfg Co, Decatur, Ill, has acquired the U B S Chemical Corp, Cambridge, Mass, and at the same time assumed all obligations of U B S.

The acquisition has been under negotiations for the past several weeks and transfers were made June 30 by company representatives according to a prior agreement. Staley delivered to U B S 102,376 shares of common stock. These shares will be distributed to U B S stockholders on the basis of one share of Staley common for each one and three-quarters shares of common stock of U B S.

The Decatur corn and soybean processor is acquiring U B S to aid Staley's research and polymer chemical development and to diversify its product lines.

Plans are for U B S to operate as an autonomous unit of the Staley Company.

Clemson Summer Course in Textiles Termed "Elongated Success"

The first summer short course in textiles at Clemson College is an elongated success—from Canada to Argentina.

Eric Cecil Johnson, Granby, Que, and George Hector Meier, Buenos Aires, were international enrollees in a three-week course in supervisor development at Clemson. Additional courses in yarn manufacturing and fabric development are in progress. Other courses will start July 15 in time and motion study, and July 27, in quality control.

TTFC Officers

The Textile Technical Federation of Canada has elected the following slate of officers and directors:

President — L J Sheps, Trilon Chemicals; *Vice presidents* — G C Tattersfield, Ayers Ltd, and J Nodtvedt, Chemcell Fibres Ltd; *Honorary Secretary-Treasurer*—G Marshall, Courtaulds (Canada) Ltd; *Past President*—S J Hungerford, Du Pont of Canada Ltd; *Directors*—A H Miller, Scholler Bros Ltd; C E Coke, Courtaulds (Canada) Ltd; E A W Boyce, Customs & Excise Branch, Canadian Dept of National Revenue; W Stansfield, Bates & Innes Ltd; C V Grantham, W J Westaway Co Ltd; Messrs Marshall, Nodtvedt, and Tattersfield; and Dr Sheps.

Armour Chemical Moves to Expand Canadian Market

In a major move to expand the marketing of its products in Canada, the Armour Chemical Division has signed a manufacturing agreement with Chemical Developments of Canada, Ltd, and appointed its own Canadian sales representative.

Under the agreement, Chemical Developments will produce at its Longford Mills, Ontario, plant many of the chemicals Armour previously supplied Canadian industry from the United States. As business conditions warrant, more of the Armour fatty acid derivatives will be produced there.

A M Stuart, formerly a technical representative for Eaton Chemical & Dyestuff Co at Toronto, was named Canadian sales representative for Armour Chemical. Mr. Stuart will headquarter at Oakville, Ontario, where Armour fatty acid derivatives will be warehoused. Additional warehouse facilities are expected to be set up throughout Canada in the near future.

15 Finishers Report Sales Growth in Scotchgard Applications

Finishers in various parts of the country are said to be enjoying a marked sales growth in applications of Scotchgard brand stain-repeller to a wide variety of fabrics, according to a recent nationwide survey.

Interior decorators are the finishers' greatest source of orders for treating fabric with the stain-repeller, while upholstery represents their greatest volume, the survey revealed.

Average percentage of the finishers' total business supplied by Scotchgard is 15.5%—although two respondents reported double this figure. Average time the finishers surveyed have been applying the stain-repeller is 1½ years.

Contacted were these 15 finishers, licensed to apply Scotchgard by its maker, the Chemical Division, Minnesota Mining and Manufacturing Co: American London Shrinkers Corp, New York; Artex Finishing Corp, New York; California Flameproofing & Processing Co, Pasadena; Fiber Cone Finish Co, Los Angeles; Geltman Sponging Co, Inc, branches in Cleveland, Los Angeles, and Minneapolis; Kiesling-Hess Finishing Co, Philadelphia; Manhattan Sponging, Kansas City; Manhattan Sponging Works, St Louis; Perma Dry Co, Inc, New York; Schwarzwaelder Co, Philadelphia; Synthetics Finishing Corp, Philadelphia; Waumbec Dyeing and Finishing Co, Manchester, NH; Western Piece Dyers & Finishers, Inc, Chicago.

Scotchgard stain-repeller was introduced for drycleanable fabrics by 3M in 1956, and for wash-and-wear fabrics in 1959.

Of the finishers interviewed, 13 use it on upholstery, 10 on apparel fabrics, seven on draperies, three on industrial fabrics, two on "any textiles," one on sheeting, and one on necktie material.

Research-Modified Flour Offers Promise of New Industrial Uses for Wheat

Wheat flour has been modified by U S Department of Agriculture chemists into products having potential uses as coatings and sizes for textile and paper manufacture, thickening agents and adhesives, it is reported.

Seeking to broaden markets for farm products, the USDA's Agricultural Research Service reportedly has demonstrated that chemically modified flour mixes readily with water to form a free-flowing paste.

Thus far, chemists at the ARS Northern Utilization Research and Development Division, Peoria, Ill, have investigated only two of a series of wheat flour modifications. One team reacted wheat flour with ethylene oxide to produce "hydroxyethylated flours." Another team employed propylene oxide as the reactant to make "hydroxpropylated flour."

The modified flours are similar to each other, and are said to differ from ordinary wheat flours in that they mix more readily with water to form pastes, and in that these pastes have less tendency to thicken and gel, thus flow more freely. They reportedly can be stored satisfactorily at a moisture content of five percent or less.

Specific research interest in wheat flour is said to be based on such inherent advantages as: 1) availability of flour as a raw material in large quantity and at a relatively low cost, and 2) the broader industrial potential of a material that combines starch and gluten, both valuable for their adhesive qualities.

Type X-7 Darvan

Development of a new, more dyeable version of Darvan nytril fiber has been announced by B F Goodrich Chemical Co, a division of The B F Goodrich Co. Called Type X-7, the new fiber modification is said by the company to be the most significant technical improvement in Darvan since its introduction late in 1955.

The Darvan X-7 fiber has undergone thorough evaluation trials to determine its spinning, knitting, and dyeing properties. According to L F Reuter, manager of fiber sales development, results to date have been excellent.

The Company states that, while pastel and medium shades of dyestuffs have been easily handled with standard methods on Darvan, the really fast deep shades to date have required a high-temperature dyeing, which has tended to restrict the range of colors available.

Darvan X-7 reportedly can be dyed a wide range of colors at the boil. Deep shades and black with washfastness can be put on Darvan at the same cost expected of other man-made fibers, it is claimed. It is further claimed that versatility has been tremendously improved in that Darvan can be dyed as raw stock, top, skeined yarn, or piece goods. Until now, knitters have primarily accomplished dyeing in the raw stock form.

The new experimental Darvan nytril fiber also is said to have affinity for a wider class of textile dyestuffs, including disperse, developed acetate, naphthol, neutral metallized, acid, metallized acid, chrome, and cationic dyes. Union dyeing with wool can be easily accomplished with the new X-7 type, it is stated.

Actual dyeing time is said to be much less with the new X-7 type of Darvan. All dyeings reportedly can be carried out at the boil in conventional equipment.

Levetrol Brine System

Morton Salt Co, 110 N Wacker Dr, Chicago 6, Ill, recently introduced Morton Levetrol, a method of liquid level control in a wet salt storage system where water level automatically is proportioned to brine withdrawn.

The Morton Levetrol System is said to be adaptable to any wet salt storage system. It reportedly protects against salt loss due to brine overflow by balancing water level with salt level, solves the problem of salt and water inventory, protects against completely drained salt storage supply, and enables complete automation of the entire water-treatment system.

Levetrol also is said to eliminate the problem of corroding float valves. All Levetrol controls are located away from the brine storage supply to avoid corrosion and assure accurate salt measurement and proper brine strength at all times.

Armour Reduces Price of Tertiary Amines

A sharp reduction in the price of tertiary amines was announced recently by the Armour Chemical Division following completion of new production facilities at the company's McCook, Ill, plant. Price reductions range from 16 to 31 percent, or from 13 to 25 cents a pound.

The new facilities and process are said to have resulted in an improved product, which makes it possible for Armour to offer tertiary amines in tank-car quantities, whereas these tertiaries were available only in limited quantities heretofore. Armour reportedly is now able to produce a line of products in commercial quantities with higher tertiary amine content and better color than formerly.

With the tertiaries available at lower costs, it is expected that many users will find it profitable to make their own benzyl quaternaries, which are useful as emulsifiers and textile softeners, among other things.

12¢/lb Price Drop in Rhoplex HA-4

Rohm & Haas Co, Philadelphia, Pa, has announced an across-the-board 12-cent per pound price reduction in Rhoplex HA-4, effective June 22. The new price of 28½ cents per pound applies to truckload lots, and smaller quantities are correspondingly reduced.

Rhoplex HA-4 is an acrylic polymer emulsion used for durable binding properties, softness and resilience in fabrics and nonwovens. Other uses of this film-forming, thermoplastic emulsion are for upholstery backing, stabilization of wool and worsted fabrics, and for improved crease recovery of rayons and cottons.

Carbolan Dyes Exhibit Compatibility with Si-Ro-Set

Resistance to shade change of the Carbolan (acid) dyestuffs when used on 100% wool garments durably creased or pleated by the Si-Ro-Set method has been cited by Arnold, Hoffman & Co, Inc, Providence, RI. With regard to shade change under this process developed by the Commonwealth Scientific and Industrial Research Organization, Arnold, Hoffman states that the Carbolan range has proven superior to level-dyeing acid dyestuffs, conventional acid milling colors, and chrome dyes.

The Si-Ro-Set solution is usually applied to dyed wool fabrics, and, as it can cause marked shade changes with certain types of dyestuffs for wool, the use of products which show the minimum shade change is desirable if shade differences between various parts of made-up garments is to be avoided. Arnold, Hoffman states that tests conducted in ICI laboratories demonstrate that use of the Carbolan dyestuffs eliminates or greatly minimizes this source of difficulty.

A complete range of shades, including fashion shades, may be obtained with the Carbolan dyes, which individually are said to be rated from "good" to "excellent" in their performance in conjunction with the Si-Ro-Set process. Ten dyes comprise the series: Carbolan Yellow 4G Conc, 3GS, and RS; Carbolan Crimson BS; Carbolan Violet 2R; Carbolan Brilliant Blue 2R, Blue B, and Brilliant Blue 2GS; Carbolan Green G Conc, and Brilliant Green 5GS.

Detailed data on the effect that the Si-Ro-Set treatment produces on wool fabrics dyed with Carbolan dyestuffs are available from Arnold, Hoffman & Co, Inc, Providence, RI.

Sandothrene Direct Black NDPN, Double Paste Ultrasperse

Sandothrene Direct Black NDPN, Double Paste Ultrasperse, a new vat black which is jet in shade, has just been released by Sandoz, Inc. Its principal use is said to be on goods which demand unusually high fastness to light, in light or heavy depths. It is being recommended by Sandoz for package dyeing, due to its small particle size. Other applications for which it is reported to be suitable are dyeing of stock, skeins, beams, and piece goods.

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...you gain absolute uniformity
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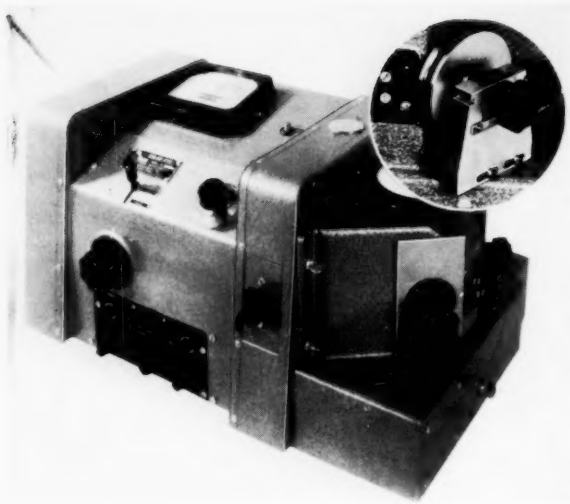
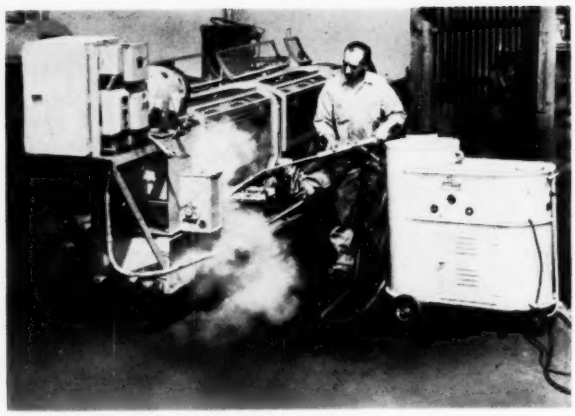
BELLE COLORS

Belle Chemical Company, Inc. / Reading, Pennsylvania / Charlotte, North Carolina

*when aftertreated with Belleloc CN or Belleloc VS





(Above): Speedysteam "100" in operation

(Left): IDL Color Eye with new sample holder shown in inset

New Sample Holder for Color-Eye

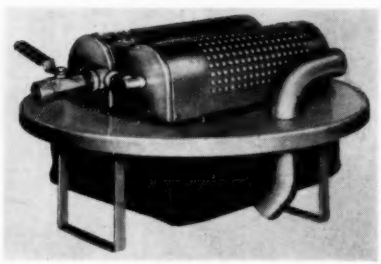
A new "spinner-type" sample holder reportedly makes it possible to measure the reflectance of colored samples of such fabrics as corduroy, gabardines, tricot knit fabrics and worsteds with directional weave, using Color-Eye, an optical colorimeter manufactured by Instrument Development Laboratories, Inc, Attleboro, Mass. It is also said to be possible to measure the color of threads, yarns and synthetic fibers wound on cards.

The new sample holder is a manually spun flywheel with concentric retaining rings for mounting samples. Other methods of mounting samples are also available. Until this special spinner-type sample holder was developed, it was said to have been generally impractical to completely evaluate or measure color on fabrics which display a highly directional surface. The new sample holder reportedly enables the instrument to view an averaged and reasonably uniform reflectance surface.

Interchangeable with standard sample holders, this new unit provides greater flexibility and a wider range of applications for Color-Eye, a dual purpose colorimeter and abridged spectrophotometer.

Vac-U-Max Twin-Jet

The new Vac-U-Max Twin-Jet, a product of Vac-U-Max, 1 Montgomery St, Belleville, NJ, reportedly combines the high suction power of standard, single-jet units now in use with doubled air volume and velocity at the suction nozzle. This is said to permit more rapid cleaning of blenders, dryers, dye kettles, etc; lint and waste pickup.



Vac-U-Max Twin Jet

Twin-Jet was developed as a quick, efficient, low-cost method for pickup of heavy objects and transfer of bulk materials. Operated entirely by air, there are no motors or moving parts.

Standard Twin-Jet units have two standard Vac-U-Max jet venturis in parallel, doubling the induced air flow through the suction hose. They reportedly operate with ½″ air line and hose (¾″ for long runs) and draw 280 cfm air through the suction hose. Velocity is said to be 11,500 ft/min through a 2″ hose. (Standard 2″ hose; 3″ hose are available.) Units reportedly fit any standard 55-gal drum. Increased filter area is provided for handling the increased air volume, cleaned by blowing back, no disassembly necessary.

Twin-Jet high-velocity units, using larger jet venturis, are said to provide even greater air volume and velocity, where special needs require more rapid pickup of bulk material. It is claimed that up to 600 cfm air flow can be provided in the suction hose. Using a 3″ suction hose, velocity is said to be approx 12,000 ft/min.

Bulletin No 101-A, covering details of the Twin-Jet, may be obtained on request to Vac-U-Max.

Speedysteam "100"

Less down-time and tie-up of production labor and equipment are required for plant and equipment cleaning, it is claimed, with a new, 100 gph, portable, oil-fired steam-jet cleaner recently introduced by Pantex Mfg Co, Pawtucket, RI, builders of the Speedylectric line of steam-jet units.

Identified as the Speedysteam "100," the unit is priced under $500 fob the factory.

Mounted on four large, rubber-tired wheels, the new cleaner is an enclosed, compact machine with built-in soap tank and controls. It reportedly can be operated on kerosene or #1 or #2 fuel oil. Ignition is automatic and fuel pressure is modulated to develop the gun-nozzle pressure desired, as shown on the gauge.

Heating coils are 0.5″ in diameter, continuous wound, and tested for 1,000 psi. Also, as standard equipment, the Speedysteam incorporates a water float tank with an antisiphon valve to assure uniform water flow and, at the same time, avoid danger of supply contamination.

It is claimed that the snap of a switch and the opening of only one valve produces adjustable, automatically controlled cleaning pressures from 50 to 150 psi in 90 seconds. Delivery at 100 gph is said to be accomplished with a quiet, rotary, valveless pump, which eliminates all pulsation and vibration.

Soap tank in the unit has a five-lb dry capacity. It is stated that no premixing is necessary and normal operation, with one filling, is six to seven hours. The unit is equipped with a ½ hp heavy-duty motor, 20 ft of wire-braided 0.5″ steam hose and racks for hose and power cord. The cleaning gun is insulated.

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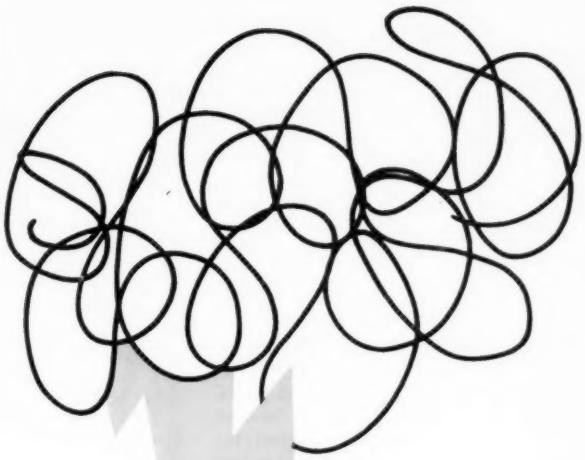

For the natural lofty Quality of undyed wool— Lyogen SMK

For perfect dyeing of wool at the isoelectric point with Lanasyn colors, Lyogen SMK insures maximum penetration of the dye, level dyeings, top fastness properties, and minimum fiber degradation.

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Sandoz
THINKS AHEAD WITH TEXTILES
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Phorwite BBU PDR, BE Pdr

Verona Dyestuffs, Springfield Rd, Union, NJ, has introduced two new brightening agents—Phorwite BBU Powder and Phorwite BE Powder.

Phorwite BBU Powder reportedly gives a neutral shade on cellulosic fibers and distinguishes itself by its exceptional solubility. It can be applied by the dyeing or pad method, and is said to offer good washfastness, thus being suitable for application in discharge printing. According to reports from Verona Dyestuffs, Phorwite BBU Powder is not sensitive to hard water, and, in fact, its exhaust is favored by electrolytes. However, it reportedly shows its best affinity for nylon at elevated temperatures at a pH of 3.5 and 4.5.

Phorwite BE Powder is said to produce a neutral cast of white and to possess outstanding solubility. Verona states that this product has excellent leveling properties, which make it of special interest for use in all applications where a short liquor ratio is involved, such as kier bleaching, package machines, beam-dyeing machines, etc.

Eversan

Eversan, an organic zinc complex antibacterial treatment developed by Ions Exchange and Chemical Corp, 48 Leonard St, New York 13, NY, was introduced to the industry at the NAMSB Fall Sportswear Panorama, May 17-21, in the New York Trade Show Building. The product is distributed in this country by Yardney Chemix Corp.

The new treatment was demonstrated as part of the display of London Handkerchief Co Inc, which is now marketing Eversan-treated handkerchiefs through department stores and other outlets.

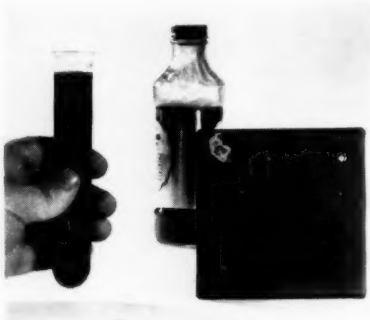
Other applications appear to be in sheets, pillow cases, shirts, underwear, diapers, and other apparel. Eversan is reported to be especially useful for "wash and wear" garments, whose lukewarm washings do not eliminate odor-causing bacterial contaminants. The product is compatible with resin finishes, and once treated with Eversan, it is claimed, these garments are able to resist bacteria even in lukewarm washings.

Eversan is said to be a completely wash-resistant treatment to inhibit the growth of a broad spectrum of bacteria, including odor-causing germs. It is claimed that the product remains effective beyond the life of any garment fabric and withstands repeated near-boiling water washes with the harshest detergents and bleaches, including chlorine.

Introduction of the new product follows seven years research and development by Ion Exchange & Chemical Corp. The product is said to have been tested against all types of bacteria, and to have proved effective against both gram-positive and gram-negative bacteria, yet safe, nontoxic and non-irritating under normal conditions of use.

In developing the product, I-X scientists made Eversan in variations for special uses depending on treating time available: slow-action types and fast-action types.

In modern plants, where the fabric travels at 125 yards a minute, fabrics subjected to the Eversan treatment for as little as half a second reportedly remained active as the fibers traveled through normal textile processing, including starch, bluing, softener and heating at 300° F. Such Eversan-treated fabrics have remained antibacterial through 75 launderings, it is claimed.



ECAC color standards

Custom Production on Color Standards

Permanent color standards designed for color matching of almost any product are now being produced by the Color Standards Dept, Erie Ceramic Arts Company, Erie, Pa. The majority of these Standards are furnished in the form of 4¼" square steel tiles with ¼" flange on all sides and finished in an acid-resisting porcelain enamel of the desired color. Due to the nature of porcelain enamel, these standards are reported to be extremely durable even under severe conditions of temperature, humidity or contact with dyes, acids, etc.

Colors are said to be fade-proof and the glass-like surface is easily cleaned as it is impermeable to staining. Matching is done from paper, plastic or other color chips or the product itself, furnished by the customer.

Reflectance standards are also available from Erie Ceramic Arts.

Ecco FM 501, 511

Addition of Ecco FM 501 and Ecco FM 511 to its growing line of polyethylene resin emulsions has been announced by Eastern Color & Chemical Co, 35 Livingston St, Providence 4, RI. Various desirable hands for fabrics are said to be obtainable through use of these products, which themselves are "designed for specific purposes" through variations in molecular weight of the polyethylene used in their formulation.

All the Ecco polyethylene emulsions are said to be anionic, but stable to acidic as well as to alkaline solutions, once they themselves are in solution. While they reportedly impart some softening to the fabrics to which they are regularly applied, in particular they are said to increase abrasion resistance and tear strength. Eastern notes that its Ecco polyethylene resin emulsions are frequently used as contributors to "wash & wear" finishes, because all the formulations in the range are fully nonchlorine-retentive.

Uses of Stearone Growing in Textile Field

Stearone is now being used in the textile industry to provide additional functional benefits to many types of fabrics according to Argus Chemical Corp, sole producer of Stearone in this country.

Laboratory tests and manufacturing results are said to indicate that Stearone's resistance to water makes it highly useful as a water-repellent coating. In addition, the product's fatty nature and lubricating properties reportedly make it effective as softening and batching aids.

Stearone, a symmetrical high-molecular-weight aliphatic ketone derived from stearic acid, is highly inert and subject to only a few reactions under vigorous conditions. It is reported to be unaffected by high temperatures, acids, alkalis and other strong chemicals; to be insoluble in water; and to have essentially no water absorption. It is also said to be incompatible with a variety of resins, polymers and organic solvents at room temperature, although compatible at elevated temperatures (thus valuable as an antiblock agent).

Technical data sheet and samples of Stearone are available by writing to Argus Chemical Corp, 633 Court Street, Brooklyn 31, NY.

• NAMES IN THE NEWS •

Rowland

Wicks

Zeno W Wicks Jr has been appointed manager of Interchemical Corporation's newly established commercial development department. **Charles S Rowland** has been appointed director of the Interchemical Central Research Laboratories to replace Dr Wicks.

The commercial development department will investigate and develop the commercial possibilities of new products and will participate in the initiation of new products projects involving research. It will also participate in the planning and investigation of acquisitions.

Dr Wicks joined Interchemical in 1944. He has held a number of posts with the Corporation, at the Central Research Laboratories and several of the divisional laboratories and production units.

Dr Rowland joined Interchemical at the Central Research Laboratories as a research chemist in 1943 and most of his early work was in the polymer field and research coordination. He served in a research capacity with Interchemical's Color & Chemicals Division from 1951 until 1954, when he returned to the Central Research Laboratories as director of the applications research department.

A Welling LaGrone has been named vice president of Seydel-Woolley & Co, Atlanta, Ga, manufacturers of textile chemicals.

Mr LaGrone joined Seydel-Woolley & Co after World War II as a trainee salesman. He very quickly showed his ability in this field, and rose to manager of sales in the Carolina territory of Seydel-Woolley's Sizing Division. Mr LaGrone will be in charge of sizing sales for the Company in the United States and Canada.

Joseph Bloom, recent honor graduate of Philadelphia Textile Institute, has joined the laboratory staff of Apex Chemical Co, Inc, Elizabethport, NJ.

Elisabeth Barabash, literature chemist at Celanese Corporation of America's Research Laboratories in Summit, NJ, is conducting classes in scientific Russian for her fellow researchers.

The first class of a dozen students started in June, 1958, meeting for a half hour twice weekly during the lunch break. A second class, started in October, still meets during the lunch hour.

The aim of her spare-time scholars, many of whom hold doctor's degrees, is to learn enough of the Russian language to translate scientific literature in their own field.

Dr Barabash is well qualified although the current classes are her first teaching experience. She is a native Russian and studied at the Moscow Institute of Technology before receiving her doctorate at the Free University of Brussels, Belgium.

Dr Barabash is shown here explaining the complexities of a Russian verb to John Clements and Thomas Dolce of the Summit research staff.

Anderson

Andrew

New technical service representatives for Chas S Tanner Co, Greenville, SC, include **Ben N Anderson** in the South and **Donald G Andrew** in New England.

Mr Anderson has been associated with the textile industry for the past 42 years as finisher and assistant superintendent of bleaching and finishing at Dan River Mills for 26 years and superintendent of Renfrew Bleachery for 16 years. He works from Tanner's Greenville headquarters.

Mr Andrew, who has been serving as sales representative for Tanner in New England for the last several months, works out of the Providence, RI, office.

Walukewicz

Lanford

Wica Chemicals, Inc, Charlotte, NC, has announced the appointment of two new men to the company staff.

Walter V Walukewicz will serve as manager of the technical service laboratories. His 12 years of experience in textile chemistry include service with Ciba, Deering-Milliken and Reeves Brothers' Bishopville Finishing Plant.

Charles G Lanford has been appointed chief chemist of the latex development and application laboratories. He has served previously with the General Latex Corp and Southern Latex Corp.

John J Barnhardt Jr has been named Atlanta dyes sales supervisor of the Southern district office of Du Pont's Dyes and Chemicals Division. **Harold L Sager** takes Mr Barnhardt's position as manager of the textile dyes section in Wilmington. Both changes were effective June 1.

Mr Barnhardt, with Du Pont since 1946, became manager of the Dyes and Chemicals Division's textile section in the home office at Wilmington, Del, early in 1958.

Mr Sager, who for the past two years has been on a special technical assignment in Wilmington, has been with the Division since 1939, except for three years of service as a naval officer.

Douglas E Campbell has been appointed secretary-treasurer of the Pulp Chemicals Association succeeding **Dernell Every**, resigned.

The Pulp Chemicals Association was formed in 1955 as a trade association of manufacturers of chemical products produced by or derived from the sulphate wood pulping industry.

Mr Campbell has broad experience in the chemical industry. He has worked with the Manufacturing Chemists' Association as assistant to the secretary; National Aniline Div, Allied Chemical Corp; Merck & Co Inc; and the Denver Chemical Mfg Co.

Mackey

Haller

Hibben

Griffin S Mackey has been employed by the Arkansas Co, Newark, NJ, in the Sales Promotional Division to cover the New York area for the promotion of Resipon NDC, the firm's new "wash & wear" resin.

Mr Mackey will also work with the Sales Division and Advertising Department in the promotion of other textile auxiliaries which the Arkansas Co has developed in the past.

Mr Mackey has had many years of experience in selling dyeing and finishing service to textile weaving mills, converters and jobbers. From 1937 to 1957, he was employed by Fair Lawn-Richmond Finishing Co, Richmond Piece Dye Works Div, working out of their sales office in New York.

American Cyanamid Co has announced the appointment of **J K Dixon** as director of research and development for the Industrial Chemicals Division and **Charles H Groezinger Jr** as assistant to the manager of the process chemicals department of the Division.

Dr Dixon joined Cyanamid in 1933 and since has served in a variety of posts at the Company's Stamford, Conn, Laboratories. In his new position, he will direct the research programs for the Industrial Chemicals Division's process chemicals, paper, and refinery departments.

Mr Groezinger, who joined Cyanamid in 1950 as a technical sales and service representative in the Industrial Chemicals Division and has since held a variety of posts with the refinery chemicals department, will maintain his office at company headquarters in New York and report to **R M Goddard**, manager of the process chemicals department.

Appointment of **Herbert Kishbaugh** to position of manager, New York sales branch of Allied Chemical Corporation's Solvay Process Division, became effective July 1. Mr Kishbaugh succeeds **Fred H Harris**, who is retiring after 34 years as a member of the Solvay sales organization.

Mr Kishbaugh had been serving as assistant manager of the New York branch office since June 1, 1958.

Herbert C Haller has been appointed an assistant to **Herbert J Wollner**, president and director of laboratories for American Conditioning House, Boston, Mass. He brings to that organization a broad background in textile processing and the application of technical controls in textile manufacture.

Mr Haller was most recently director of research for Bernhard Altmann International Corp, where he directed the development of new processes and products and the installation of quality control systems at the Corporation's plants in Vienna and the United States. He was also responsible for new procedures and quality control in production commissioned to plants in Switzerland, England and this country.

Mr Haller will deal with technical problems concerned with manufacture. He will also contribute to the American Conditioning House advisory program in connection with the new labeling laws for all types of natural and man-made fiber products.

Mr Haller will make his headquarters at ACH's main laboratory at 11 Melcher Street, Boston.

OBITUARY

JAMES H HIBBEN

JAMES H HIBBEN, chief of the Chemical Division of the Tariff Commission, and one of the foremost chemical consultants in the United States, died suddenly at George Washington University Hospital, after a fall at his home, 5716 El Nido Road, McLean, Va.

Dr Hibben was born in Indianapolis, Ind, on May 14, 1897. He attended public schools in Indianapolis; was a graduate of the University of Illinois, receiving his B S in 1920 and his M S in 1922; and the University of Paris (1924) with a degree of D Sc. He has been a fellow of the International Education Board at Paris (1924), a National Research Fellow at Princeton University (1925-27), consultant to the Bureau of Standards and to various chemical industries, and a member of the research staff of the Geophysical Laboratory of the Carnegie Institution of Washington (1928-1939).

During World War I, Dr Hibben enlisted in the Army as a private and served with the AEF, being discharged in 1919 with the rank of sergeant.

Dr Hibben was a member of the Washington Academy of Sciences (vice pres); New York Academy of Sciences; the Cosmos Club (Washington); American Chemical Society; the Chemical Society of Washington (treas, sec, pres; Hillebrand Prize award); Sigma Xi and Sigma Chi; and a former Fellow of the American Institute of Chemists.

He was the author of several books and many papers. One of his best-known works was the book entitled "The Raman Effect and Its Chemical Application" (1939). This was one of the first definitive works on this subject. It brought together all the then-known information on a new type of secondary radiation information by which the behavior of atoms within the molecules and the molecules themselves may be determined independently of their state of aggregation. Many applications of this effect have been made, both to physics and chemistry, and Hibben's "Raman Spectra" is still used as the starting point for much of this work.

Since going with the US Tariff Commission in 1939, as chief of the Chemical Division, Dr Hibben carried out many complex and important responsibilities which, by law or Executive order, the Tariff Commission is charged with making. He provided basic and authoritative information to the Commission, to top-ranking officials of Government agencies, executives of industry, and, when necessary, to members and committees of Congress and the Office of the President on matters relating to US tariffs and foreign trade pertaining to chemicals and chemical products. During World War II he was chairman or member of many intra-agency committees and commissions.

He was directly responsible for the organization and publication of the Tariff Commission's annual report on "Synthetic Organic Chemicals, US Production and Sales."

NORMAN PETERKIN

NORMAN PETERKIN, 75, retired advertising director for General Dyestuff Co, died May 17 after a short illness in Mountainside Hospital, Montclair, NJ.

A native of England, Mr Peterkin retired eight years ago. He had been with GDC for 15 years and prior to that with United Piece Dye Works, Lodi, NJ, for about 20 years as purchasing agent.

ALFRED R MACORMAC

ALFRED R MACORMAC, 64, associate professor of chemistry at the School of Home Economics, University of Alabama.

Dr Macormac was an active AATCC member, having served on several committees for the preparation of papers for the Intersectional Contest.

From 1942 to 1949, he served as a textile technician for the Army Quartermaster Corps, and until 1955, served the US Dept of Agriculture as textile chemist. He joined the Alabama faculty in 1955.

Dr Macormac also served as a professor of textile chemistry at Clemson College and Alabama Polytechnic Institute, and chief chemist of Textile Products Co, Greensboro, NC.

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